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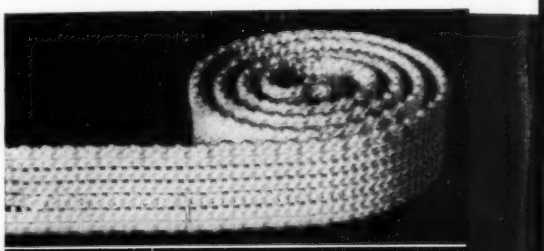

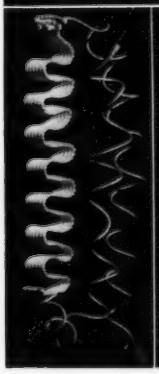

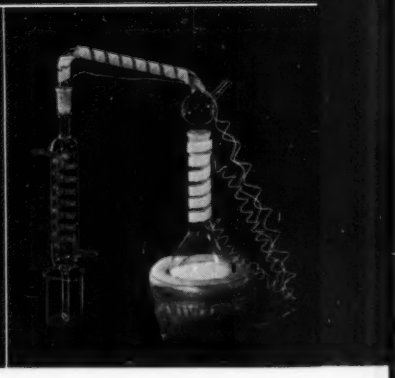

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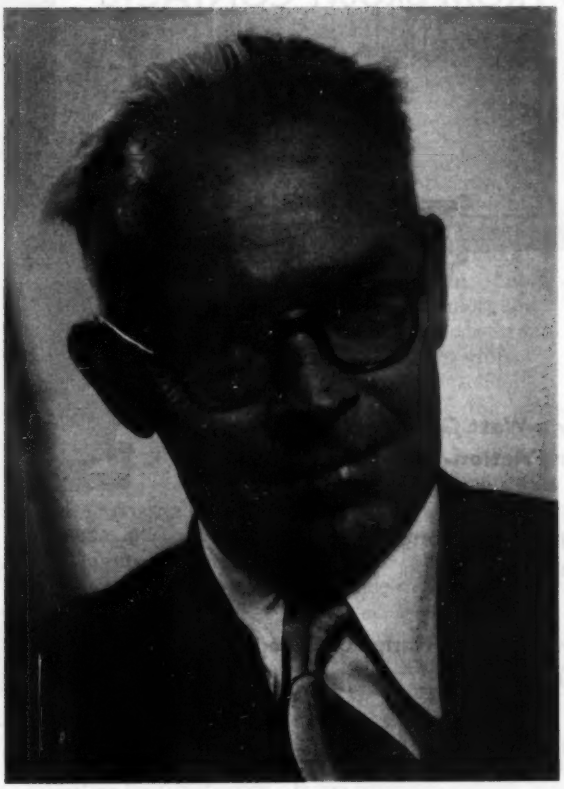

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(See page 357)

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Editor's Outlook

WHAT makes a good college teacher? Well, what 820 college administrators *think* makes a good teacher is revealed in a report discussed in a recent number of the *Journal of Higher Education*.[1] The details of the study are not described but it seems that a large number of college presidents and other executives were asked to express their opinions of some 52 "desirable characteristics" of college teachers. Though we resist the temptation to argue whether or not this is a good way to reach an answer to the question, we may nevertheless interest ourselves in some of the conclusions that emerge.

Only ten of the "desirable characteristics" under consideration refer to the teacher *as a scholar*. And of these, only one is thought to be "highly important" by even a majority of the referees—"Having an unusually high academic record in his special field." Nevertheless, sixteen characteristics of other than scholarly significance were considered highly important. All the traits most valued were in some way related to interest in, understanding of, and stimulating influence upon college students. Among the characteristics which were more acclaimed than high scholarship were: "Inspires students to think for themselves and to express their own ideas sincerely." (Highest rating of all.) "Is emotionally stable and mature." "Is friendly, democratic, tolerant, and helpful in his relations with students." "Behavior reflects high ideals." "Has a genial personality and sense of humor." "Organizes materials and prepares carefully for each meeting of his class." "Has successfully taught his subject in college." "Takes a broad, rather than a departmental, view of educational problems."

All this sums itself up in one "highly important" characteristic: "Regards himself as primarily a college teacher rather than a subject-matter specialist."

The expressed opinions of 820 of our educational "bosses" cannot be lightly disposed of—even if we might want to do so. Should we tell our graduate students, preparing themselves to take the thousands of academic positions which are (or soon will be) waiting for them, that they should strive to develop a sense of humor and the technique of organizing daily lessons rather than put their main energy into mastering their subject? What a jolt for the morale of the graduate school!

One-sided as the comparison seems to be, there is something here which our young aspiring teachers should be aware of. If he has no interest in students for their own sake, no understanding of them or desire to stimulate them, a young man should *not* be encouraged to make a career of college teaching. There are other, more productive outlets for his scholarly talents. Fortunately, the choice is seldom if ever on a purely "this-or-that" basis, but rather "a little of this" *and* "a little of that."

Which way would the administrator turn if he were faced with a choice between (*a*) the brilliant but self-centered young man who passed his Ph.D. examination with the highest honors and has seven publications to his credit, but who dislikes to have anyone working with him, who locks his office door when his lecture is over and passes other students without recognizing them; and (*b*) the man who passed his final examinations only after the third trial and was given his degree to get rid of him (after half his language requirement had been waived) but who gets the students in his laboratory section so interested in the things *he* doesn't know that they stay long after hours and come to his office to pester him about their troubles in other courses.

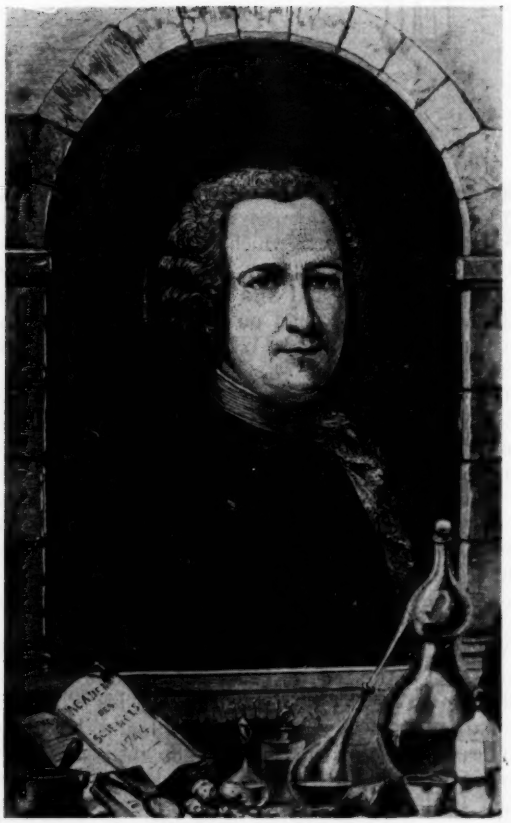
The choice depends upon the position he will occupy. The former young man might very well get an appointment involving teaching and research at the graduate level, where his students may, if necessary, survive upon nothing but intellectual stimulation. And perhaps the young man might himself be cut down to size by continual association with his intellectual equals and superiors.

[1] TRABUE, M. R., "Characteristics desirable in college teachers," *J. Higher Educ.*, **25**, 201 (1954).

(Continued on page 343)

THE LECTURES OF GUILLAUME FRANÇOIS ROUELLE

PIERRE LEMAY and RALPH E. OESPER
Nice, France, and
University of Cincinnati, Cincinnati, Ohio



Guillaume François Rouelle

ROUELLE was an unusual and picturesque character. However, neither his occasional bizarre behavior nor his scientific accomplishments, which had considerable merit, would have sufficed to save him from the semi-oblivion which is the standard fate of all except the outstanding chemists. It was his fortune to have taught a number of exceptional students, particularly Lavoisier, and so he has shone by reflected glory. It would be difficult to find among chemists two more different personalities than Rouelle and Lavoisier. One, a dynamic teacher, volatile, unmethodical, impetuous, a kind of impecunious Bohemian of science; the other a painstaking investigator, sedate, aristocratic in bearing, a wealthy amateur. Perhaps it was the attraction of opposites that led Lavoisier to so spectacular a lecturer, possibly it was because Lavoisier's favorite teacher and mentor, Guettard, was also an unorthodox, brusque character.[1]

Guillaume François Rouelle, usually referred to as the elder (*aîné*), was born on September 15, 1703, in the village of Mathieu, not far from Caen, in Normandy. His parents were Jacques and Marie (*née* Bougon). Bright and industrious, he made a good record at the Collège Du Bois in Caen. He early developed a liking for natural science and on his vacations collected plants that were new to him and transplanted them to the family garden. He easily obtained the *maîtrise ès arts* (roughly equivalent to the present bachelor's degree) and started the medical course. However, he was not happy with this choice, largely because he was too sensitive. He turned to chemistry, which had appealed to him from the start. For laboratory purposes, he used the neighboring smithy, and enlisted a younger brother as assistant, but the latter proved inept. He was replaced by another brother, Hilaire Marin (1718–78), who as Rouelle the younger (*le jeune*) also made a name for himself as a chemist.

Quickly realizing that the training necessary for success in his chosen field could be obtained only in Paris, Guillaume, accompanied by two equally penniless companions, went to the French capital. For a while they hungered together, and then Rouelle was fortunate to secure an apprenticeship under Spitzley, a German apothecary, a successor to the famous Lémery. Rouelle remained in this post for seven years, learning not only pharmacy but also chemistry, botany, and natural history, since he was given every opportunity to attend lectures and demonstrations in these fields, which were so closely related to his principal subject.

He was an apt student, built up a favorable reputation among his teachers, and organized a private course in pharmacy and chemistry. In 1742 he was appointed *demonstrateur en chimie* at the Jardin du Roi, succeeding Boulduc (1675–1742). The official appointment was

[1] There are several accounts of Rouelle's life. Most of them are based on the "Éloge" by Grandjean de Fouchy, Histoire de l'Académie, **1770**, and GRIMM, F. M., "Correspondance littéraire," **1812**. See also CAP, A., "Études biographiques pour servir a l'histoire des sciences," **1857**, 253–6; *Journal de Pharmacie et Chirurgie*, September, **1842**, revised in **1857**; HOEFER, L., "Histoire de la Chimie," **1886**, Vol. 2, pp. 378–83; DESTREE, P., *Bull. de la Société d'Histoire de la Pharmacie*, **1817**; DORVEAUX, P., *ibid.*, December, **1933**; SCHOFIELD, M., *Pharm. J.*, **161**, 199 (1949); LEMAY, P., *Bull. Soc. Histoire Pharm.*, March, **1949**; MCKIE, D., *Endeavour*, **12**, 130 (1953).

dated June 9, 1743. On May 7, 1744, he was admitted to the Académie Royale des Sciences as adjoint chemist; promotion to *associé* came on July 16, 1752.

At the Jardin du Roi, the chemistry lectures were delivered by the rather dull Bourdelin (1696–1777), who was often temporarily replaced by Malouin (1701–77) or Macquer (1718–84). The demonstrator was supposed to reinforce what the lecturer had stated, but Rouelle frequently endeavored to prove the precise opposite. The entertainment he provided and the undignified events that sometimes highlighted these lecture demonstrations have been described in all the biographies of Lavoisier.[2]

In 1746 Rouelle moved his now much enlarged laboratory and private lectures to the Rue Jacob, and in 1750 he set up a pharmacy there.[3]

A prospectus, dated 1759, outlines Rouelle's lectures:

> The plants, animals, and minerals are the subject of these experiments; they are divided into three parts.
>
> *Part One:* Examples will be given of the various ways of analyzing plants, of extracting from them oils, essential salts, and fixed salts, and of making extracts from them; we will then proceed to fermentation and spiritous liquors.... The various combinations of vegetable substances will be shown, such as the oils with alkalies and tartrous salts rendered soluble by other salts or by earths.
>
> *Part Two:* Animals are the subject of the second part... They will be analyzed and several substances derived from them.
>
> English phosphorus, which up to the present has been known to only very few persons, and which is the product of the final violence of fire, will be the subject of most unusual experiments at the end of this part.
>
> *Part Three:* In this part, there will be treated the substances derived from the bowels of the earth, which are called minerals. This part is one of the most prolific in experiments.
>
> The analyses of bitumens, nitre, etc....will be conducted with exactitude, to them will be joined the recomposition of these salts...fermentations hot and cold, the change in color, detonations and the production of flame are all effects of these mixtures that will be discussed.
>
> We shall conclude with the vitrification of metals, the colored glasses, the volatilization of metals and several unusual procedures which throw light on the nature of substances.

A learned course, no doubt, but a little banal. It was, it seems, an unforgettable sight to see this robust Norman, with ruddy complexion, red hair poorly concealed beneath his askew wig, delivering his opinions and conducting his demonstrations with as much vehemence as a lawyer in the midst of a heated trial. When he found them too much of an encumbrance, he divested himself, one after the other, of his coat, vest, and wig.

Publishing little, he often inadvertently revealed his "secrets" to his audience and then was astounded to hear them being discussed. In a manuscript copy of his 1761 lectures it is stated with respect "to vitriolic ether, which he claimed to have been the first to discover a method of preparing in large batches, a secret long concealed by the Italian Marsini," that he, Rouelle, had quickly succeeded in solving this problem and that he had been selling this product at a moderate price for a long time and making a fair profit. However, he did not disclose his method, in either his public or private lectures, until 1754. Consequently, when the very next year Baumé read a paper before the Académie containing much of the same information that Rouelle had already revealed, Rouelle was infuriated and accused Baumé of plagiarism: "this discovery is mine alone, he has stolen it from me." The notion that others were appropriating his ideas became an obsession with him; he employed the epithet "plagiarist" on all sorts of occasions and at the least provocation. For example, the well known physician Bordeu (1722–76) had treated Rouelle's brother successfully for a serious illness but Rouelle did not approve of the measures employed. Each year thereafter, at a certain point in his lectures, Bordeu received a stinging rebuke and the audience was highly amused when the chemist declared, "Yes, gentlemen, it was one of our own kind, a medical man, a plagiarist, who killed my brother," and the hilarity was heightened when the brother, in the best of health, then appeared at the door. On another occasion the eminent Buffon (1707–88), who usually was most sedate, amused himself by sending Rouelle a pretended dissertation on "The anatomy and organization of the centaurs." That same day, Rouelle told everybody that this work did not contain a single line that had not been brazenly stolen from his own lectures or publications.

However, such eccentric conduct and wild statements must not be allowed to blot out the fact that Rouelle was really an able scientist, capable of useful and original ideas. His researches contributed to the analysis of natural materials; he sought to establish a rational classification of compounds; he tried to unravel the mystery of the combination of acids and bases by separating the salts into neutral, acid, and basic. He, along with Macquer, introduced into France the phlogistic hypothesis, which was the best attempt, up to then, to bring into chemistry the unifying principle it had always lacked. He should also be remembered as the trainer of successful men of science, and without appearing arrogant he justifiably exclaimed repeatedly: "Listen to me, I am the only one who can demonstrate these truths to you." Among his disciples were such luminaries as Diderot, Bertrand Pelletier, Proust, Darcet, Bucquet, Leblanc, Lavoisier, etc. In his "Tableau de Paris," Mercier declared:

> Whoever has not heard Diderot and Rouelle does not know the power of eloquence or the heart-stirring form of enthusiasm; he does not appreciate how one man can gain mastery over another. Of all the men I have heard in my lifetime, the most eloquent were Rouelle and Diderot... When Rouelle spoke, he inspired, he overwhelmed; he made me become fond of an art of which I had not the least understanding. Rouelle enlightened me, he

[2] See PARTINGTON, E. J., "Makers of Chemistry," **1931**, p. 189; FIGUIER, L., "Vies des Savants illustrés," **1874**, Vol. 5, pp. 433–43.

[3] After his death the business was carried on by his widow, assisted by her son and brother. In 1794 she sold the establishment to Bertrand Pelletier, her former manager; his grandson, the famous Joseph Pelletier, codiscoverer of quinine, received some of his training there. See DELÉPINE, M., J. CHEM. EDUC., **28**, 454 (1951).

subjugated me; it was he who made me a devotee of that science which will assuredly regenerate all the arts, one by one. Since that time, chemistry fills me with veneration; without Rouelle I would not have been able to see beyond the apothecary's mortar.

Rouelle's conscientiousness asserted itself in even the smallest details. For example, his brother states in his "Tableau d'analyse chimique" (Paris, 1774):

He felt the necessity of presenting to his listeners a short but clear table of all the operations which formed the sequence of his demonstrations and served as the basis of his doctrine. He believed that there was no more suitable way of achieving this objective than to exhibit at the same time bottles and glass jars containing all the quite distinct and well prepared products of each operation; the labels he pasted on the containers carried a brief but clear indication of each of his experiments and the results obtained from them; he called them *Procédé du Cours de Chimie.* Since these *procédés* did not always follow the order and progress of his lectures, he had them placed, as they increased in number, on the shelves in his laboratory, to remain there until the course was completed. Experience showed the usefulness of this exhibition to his listeners. They found there a very brief but understandable repetition of what they had previously seen, the operation being repeated as it were a second, a third time, in a word, as often as they wished.

It is easy to understand how such lectures and such a personality would make a lasting impression on young men eager to make a career in science.

It is unfortunate that these dynamic lectures were never put into print. Toward the end of his life, Rouelle made preparations to publish his "Cours complet de Chimie," and word of this intention got out. It was then that he refused to give the publication rights to an English house, whose offer topped the best Paris figure by 500 louis. After his death, his heirs, *i.e.*, his brother Hilaire Marin and his son-in-law Darcet, began to assemble the material with the intention of completing and then publishing it. In this connection they inserted a notice in the October, 1770, issue of the *Journal de Médecine, Chirurgie et Pharmacie:*

The reputation which the late M. Rouelle built up by his courses has led those who attended them to assemble all they could take down of his lectures: several of his disciples have even taken the trouble to collect the greater part of these scattered fragments and to put them into bound forms, which were passed from hand to hand and which more than once have been the object of attempts some day to bring out printed copies. His family justly fears that some time someone will succeed in publishing these lectures but only in a still more defective form because of the errors that eluded the editors; it is impossible that these will not be augmented by a large number due to the copyists. We therefore feel that it is our duty to announce that we are now actively collecting all the papers, notes and remarks left by the late M. Rouelle, and are planning to set these in order with the intention of publishing them ourselves. The family believes it all the more necessary to make this announcement since they fear that the unwise zeal of some disciple of this famous man will bring harm to his reputation while believing that he is enhancing it.

No one knows what happened to this plan. However, there are in existence many handwritten copies, drawn up directly by some of his listeners, or copied from the Diderot manuscript. Etienne Charavay, the expert on autographs, once had in his possession a manuscript copy (614 pages, folio) entitled: "Cours de Chymie ou Leçons de M. Rouelle recueillies pendant les années 1757 et 58 par M. Diderot (copie sur l'original écrit par la propre main de Diderot)." This is valuable because it fixes the dates when the great philosopher attended Rouelle's lectures. Copies are preserved at the Bibliothèque Nationale in Paris, at Bordeaux, and at Clifton College (near Bristol, England). A copy, in the hand of one Dr. François Baraillon of Montpellier, is owned by the senior author; it has 592 pages, folio. Copies drawn up by other students are known, at the Faculté de Pharmacie de Paris, for instance. The Lemay collection contains two anonymous copies; one, "Cours de Chimie de M. Rouelle pour l'année 1761" (989 pages, quarto), is very carefully prepared; the other, somewhat shorter, is in two volumes (338 and 259 pages, duodecimo).[4]

Diderot called on his general learning and added a historical part to the "Introduction of Rouelle's Course;" the portion devoted to the utility of chemistry is merely a development of the lecturer's text.[5] We prefer the 1761 text in the Lemay collection; it seems to be free of all foreign embellishments, the editor limiting himself to a few notes written in the margins.

Rouelle's chemistry was still based on the four-element theory, namely, fire or phlogiston, earth, water, air. He suspected that there might be a fifth element, doubtless the mercurical principle of Becher. However, he declared: "These principles of themselves do not form compounds directly as Aristotle taught of his elements and Epicurus claimed for his atoms, but several other elementary substances of different nature come together and form mixtures." Although the possible number of such combinations was high, he believed that the actual number of these *mixtes* was small and that not more than ten or twelve were known. Several *mixtes* of different kinds when joined together produced compounds. In short, these *mixtes* were nothing else than our simple substances. He also affirmed the conservation of matter and the immutability of the elements.

Our first chemists and early philosophers had but little knowledge of combinations and this was the source of their errors and their systems concerning the loss of form, the penetrability of matter, etc. . . . illusions just as fruitless as the debates they engender. They believed that it is impossible to demonstrate the true principles because the bonds are so intimate that they can never suffer perfect disunion. If sometimes our efforts succeed to the point of disuniting these substances, they suddenly attach themselves to others and form a new *mixte* or produce new compounds. It is from this new combination that chemistry obtains its insights; it is by the transfer of this principle from one *mixte*

[4] The Lemay collection also contains notes taken during a course on pharmacy (likewise unpublished); no other copies of this seem to be known. It was written out by one Fournier, Maître en Chirurgie at Gisors. It has 596 small pages plus plates and an index; the date is 1748. The last 64 pages are devoted to affinity tables of Geoffroy, the elder.

[5] See HENRY, CHARLES, *Revue Scientifique*, July 26, 1884, and June 27, 1885; also his "Introduction à la Chimie, manuscrit inédit de Diderot, publié avec notice sur les cours de Rouelle et tarif des produits chimiques en 1758" (Paris, 1887, 108 pages).

into another that we discover its properties; we allow it to pass successively into several compounds, which proves to us that they are indestructible, immutable and indivisible.

An excellent method of approach, which has since been widely and successfully applied. All through Rouelle's lectures there are ingenious ideas, some of them rather striking analogies to modern theories.

In the chapter on fire he explains how the heated globe alternately expands and contracts on contact with the air,

from which it results that this globe and the air surrounding it are in a perpetual state of systole and diastole, the cause of the alternate emission and return of the light rays, which are the same as those of fire. According to M. Rouelle, all the phenomena of electricity have a similar cause, and he is convinced that all substances are electric.

This same heated globe supplied the explanation of the future experiments of Montgolfier with hot air balloons:

The surrounding air rarefied by the heat of the globe expands and tries to extend itself, which makes it rise. The lower air which takes its place, being colder, produces a current from the lower part to the higher, which carries the heat toward the top. Thus experience shows that all burning bodies are always hotter at their upper part than anywhere else; it is this current of air and heat which provides the movement to the little windmills which children place alongside the stove pipes.

Another passage anticipated Herschell and Melloni:

There is no doubt that the various reflections and contractions undergone by the sun's rays in our atmosphere contribute to the intense heat that is experienced at certain places and on certain days; however, this heat is augmented considerably by the reflection of the light by certain objects; furthermore, the heated bodies themselves also act as hearths which increase the heat by their activity. In fact, it appears that this is the chief cause of heat in our atmosphere, since on the mountains, where the solar rays are almost pure, the heat is very much less.

In the chapter on air, there occurs a very judicious remark: "A great many phenomena are attributed to the air with which it has nothing to do. For example, it is regarded as the material of the bubbles that are seen in boiling water, bubbles which M. Rouelle believes are produced by a fluid made to expand in another fluid—these are the molecules of the water itself reduced to vapor." Also: "M. Rouelle is very sure that in absolute cold the air will take on a concrete form." Contrary to most physicists of his time, who believed that the atmospheric air contained quantities of substances,

he regarded this chaos as a chimera and he claimed that, with the exception of a small number of these materials, all the others fall almost as soon as they have ascended; they cannot remain in the atmosphere, and hence the space they occupy is very circumscribed and limited to the place where the evaporation occurred. He thought that if the air was as the physicists described it, it would be absolutely unfit for respiration.

Rouelle believed that storms are the chief purifying agents of the atmosphere.

An able laboratory man, Rouelle paid special attention to equipment and apparatus. He was particularly interested in distillation devices and furnaces, since they were the chief aids in the analytical procedures of the time. He profited greatly from his contact with Duchesne, a potter and builder of furnaces, whom he met in the laboratory of the Duc d'Orléans in the monastery of Sainte Geneviève. This able workman, who claimed that he had learned his trade in Barbary where he also probably learned his drinking habits, was the delight of the courtiers of the Prince, because of the incredibly foul expressions with which he peppered his conversation.

His experiments involving the collection of gases led Rouelle to devise an apparatus for that purpose:

It has been a long time since chemists first attempted to seize on the air which enters into the combination of substances.

An Impressive Demonstration in Rouelle's Lecture

Boyle was the first to make such trials and to succeed in measuring it. Mariotte likewise studied this material at great length; but it is to M. Hales that we owe an apparatus suitable for the complete measurement. Although his device was somewhat defective, its basic principles were simple and easy to understand. Consequently, it was not difficult for M. Rouelle to correct it. Here is the apparatus which he used: he took a tin siphon, similar to the second model of M. Hales; in its bend he inserted a round vessel about three inches in diameter. The small branch of his siphon is the one which received the neck of the retort; it is very short and twice as big as the other which is about two feet high. When he wishes to use it, he cements the neck of the retort to the small branch of the siphon; he uses for this purpose his fatty lute, and makes the joint above the wetted vessel, making several turns with cord to ensure a tight fit. He then immerses the siphon in a trough of water in such wise that the joint between the vessels is below water. He places above a large glass receiver, which is supported on the four uprights soldered to the vessel just mentioned and which encloses the large branch of the siphon. He then pumps the air from the receiver through a small hole that he has left in its upper part, and when he has sucked out with his mouth as much air as possible, he closes the hole with lute and marks the place to which the water has risen. Then he distills the air which is released from the substance and this expands into the vacuum, causing the water to fall. The space between the mark and the place to which the water has fallen is the measure of the quantity of air.

It may well be asked why Rouelle did not simply cap his siphon with a tube filled with water; this would have enabled him to collect a pure gas and to avoid the aspiration.

After the preliminary lectures came the detailed study and analysis of the various substances making up the three natural kingdoms. He began with the vegetable kingdom. In his discussion of the extraction of essential oils and perfumes he used a very nice expression; he referred to a procedure of this kind as "giving them wings."

It was in connection with "tartar" (potassium sulfate) that he gave his classification of salts into neutral, acid, basic—a classification that has become classic. This topic has been discussed by so many others that there is no point in elaborating on it here except to emphasize that he was the first to speak of a salt, a term that had previously been employed very vaguely, as the product of the union of any acid with a *base*, a term used by him to include alkalies, earths, metallic substances, and oils. He stated distinctly that a definite quantity of acid always combined with a definite quantity of base, no matter which of the three classes of salts was produced.[6] It is to be noted that his ideas were not accepted immediately, but, being founded on good experimental evidence, they eventually came into their own.

He then went on to the animal kingdom. Here again he made original studies because no one understood the chain of phenomena involved.

With respect to the mineral kingdom:

M. Rouelle believes that the aptitude to crystallize is universally distributed in the mineral kingdom, that there is no material that is not susceptible to crystallization. He claims that even the most unformed rocks have a core or base consisting of a regular crystallization and that this can be uncovered by dissecting and anatomizing the materials, so to speak. Their parts are united not by intussusception but simply by juxtaposition; by applying one to the other, they observe regular figures and form crystallizations.

Haüy later demonstrated this definitely.

He was quite clear as to the difference between primitive and sedimentary terrains and stressed the geological revolutions undergone by the earth. Referring to fossils he said: "The organization of these creatures is still so apparent that there is no room for doubt about their origin or for notions that they are simply jests of nature."

He attributed volcanic phenomena to the meeting of internal fire with large quantities of water that had penetrated into cavities of the earth. The phenomena of erosion were neatly summed up. "The waters of the rains and those of the rivers produce changes in the surface of the earth that are not less considerable than those due to the sea, a fact that indicated to M. Rouelle that the surface of our globe is in a state of continual destruction."

On the other hand, Rouelle's lectures contained the errors inherent in the science of his time. However, his mind was flexible and he was ever ready to learn new facts. Had he lived long enough, he surely would have been the first to adopt the theories of his illustrious pupil. It is equally certain that he would also have accused Lavoisier of plagiarism.

Rouelle's skepticism about the teachings of his predecessors appears very plainly in the chapter on alchemy.

This is all that M. Rouelle told us about transmutations, which so many discuss without real knowledge. As to his own views, although he does doubt the testimony of the great men who declare that they have witnessed transmutations, he is most anxious to see one so that he may be relieved of the doubts he still retains.

Rouelle's lectures deserve a more extended analysis than they have been accorded thus far; perhaps they merit full publication with a commentary by a competent authority. However, it is hoped that the present reader will be left with the impression that Rouelle was endowed with a truly original mind; that he was an outstanding teacher and a fairly important scientist, who had the misfortune of being overshadowed in his own time by the better known Macquer and who, after his death, was so outstripped by his pupil Lavoisier and the triumphs of the new chemistry that his merits and achievements have been unduly and unjustly disregarded.

Rouelle's pharmaceutical career likewise deserves notice, despite the fact that he was forty-seven years old before he received the title *maître apothicaire*. Some time later, when the place of *premier apothicaire* to Louis XV became vacant, it was offered to Rouelle by the Duc de la Vrillière, Minister of the King's Household, and his colleague in the Académie des Sciences. Despite the high income attached to this

[6] For discussions of Rouelle's ideas concerning salts see HOLMYARD, E. J., "Makers of Chemistry," **1931**, p. 194; WALDEN, P., "Salts, Acids and Bases," **1929**, p. 47; KOPP, H., "Geschichte der Chemie," **1845**, Vol. III, p. 67.

post, Rouelle refused it because he knew that he would be ill at ease in court circles and especially because he would have to give up his lectures and his laboratory, which were the focal points of his whole existence. However, in 1753 he did accept an offer to succeed Claude François Geoffroy as *inspecteur général de la pharmacie* at the Hôtel Dieu. Here he immediately showed his unselfishness and scrupulous honesty; he opened his regime by abolishing the long-standing custom of accepting gifts from the tradesmen who supplied this large hospital. For the benefit of the patients, he quickly established the position of *premier apothicaire*, who was made responsible for the promptness and efficiency of the service.

Not long after he read his famous paper on neutral salts before the Académie (April 24, 1754), he was assigned by the Minister of War to examine a proposed new method of making and refining saltpeter. This brought him much labor and no profit, because the author of the process had influence at court. The resulting anxiety and fatigue marked the start of Rouelle's nervous ailments. Nonetheless, the next year he accepted the burdensome task of studying the assay of the gold coinage. Once again he emerged from a well performed assignment thoroughly exhausted, and also with a new disappointment because he had been promised the post of chief assayer, a promise that was not kept. From this time on he found it necessary to remain within his cramped living quarters. Since he could no longer attend the meetings of the Académie, he refused to be a candidate for the vacancy as *pensionnaire chimiste* at the death of Hellot in 1766. He resigned his post as *demonstrateur* at the Jardin Royal in 1768; he was succeeded by his brother Hilaire Marin. Six years of severe pain left him a paraplegic. In the hope that a change of air would be beneficial, he was moved to the suburb of Passy, where he died on August 3, 1770.

Of his twelve children, only a son and a daughter survived him. The daughter married the chemist Jean Darcet (1727–1801) in 1771; their son, Darcet *fils*, also made a name for himself in chemistry.

Rouelle's published papers were few. They were as follows:

(1) "Mémoire sur les sels neutres, dans lequel on propose une division méthodique de ces sels, qui facilite les moyens pour parvenir à la théorie de leur crystallisation," *Histoire de l'Académie Royale des Sciences*, **1744**, 353–4.
(2) "Sur le sel marin. Première partie. De la crystallisation du sel marin," *ibid.*, **1745**, 57–79.
(3) "Sur l'inflammation de l'huile de térébenthine par l'acide nitreux pure, suivant le procédé de Borrichius, et sur l'inflammation de plusieurs huiles essentielles et par expression avec le même acide, et conjointement avec l'acide vitriolique," *ibid.*, **1747**, 34–56.
(4) "Sur les embaumements des Égyptiens. Premier mémoire, dans lequel on fait voir que les fondements de l'art des embaumements égyptiens sont pour partie contenus dans la description qu'en a donné Herodote, et où l'on détermine quelles sont les matières qu'on employait dans ces embaumements," *ibid.*, **1750**, 123–50.
(5) "Mémoire sur les sels neutres, dans lequel on fait connaître deux nouvelles classes de sels neutres, et l'on développe le phenomène singulier de l'excès d'acide dans ces sels," *ibid.*, **1754**, 572–88.
(6) "Précis des embaumements," *Journal de Médecine et Chirurgie, Pharmacie*, **1756**, 299–304.
(7) "Analyse de l'eau minérale de M. et Mme. de Calsabigi, nouvellement découverte en leur maison de Passy, par M. Rouelle apothicaire de la ville de Paris, demonstrateur de chimie au Jardin Royal et membre de l'Académie Royale des Sciences," *ca.* **1753**, pp. 3–11 of 29-page brochure, "Analyse d'une eau minérale faites par MM. Rouelle et Cadet."

Editor's Outlook

(Continued from page 337)

But for a college job any administrator would—if he has to—take a chance on the second. He doesn't need to be so *far* above his students to inspire them. He may do it better if he comes nearer to being one of them. Furthermore, he is only beginning at this stage; he still has a long time in which to grow. A young teacher can make up (or cover up) his scholarly deficiencies more easily than his human, emotional, and spiritual ones.

But contrasts as extreme as this are rare. We forget (or fail to observe) that by far the most frequently, ability in one direction goes along with that in another. The qualities necessary for a good teacher most generally *do* accompany high scholarship, and we can usually have some of both.

Nevertheless, as is pointed out in the article cited, our graduate schools are either not aware of these facts of academic life, or if they are, they are too stubborn to try to do anything about them. Tens of thousands of new college teachers will be needed within the next few years; are we to depend upon their being *born*, without our trying to do anything about *making* them? To be sure, we can scarcely give them courses in developing a sense of humor, an inspiring personality, and high ideals, and other such characteristics thought desirable, but we can do more to emphasize the importance of these things, and especially the importance to the young teacher of thinking about other things as well as his subject matter.

The "subject-matter" graduate schools must recognize the state of affairs, else there will be more and more of our young prospective college teachers who will be led to take their graduate degrees in "education," and this is not a movement which we would like to see gain headway in the field of science, if we can believe the general consensus.

THE MECHANISM OF DIAZOTIZATION

RICHARD G. GILLIS
Melbourne Technical College, Victoria, Australia

ALTHOUGH the diazotization reaction was discovered by Peter Griess in 1858 and its applications were extensively investigated by many workers, it was not until 1899 that the first mechanistic study was carried out by Hantzsch and Schumann (*1*). They found that the reaction was what would now be called second order and expressed the results in the rate equation

$$\text{velocity} \propto [\text{R—NH}_3^+][\text{HNO}_2] \qquad (1)$$

Since that time a great number of other investigators have supported Hantzsch's conclusion, including Tassilly (*2*), Boeseken and Schoutissen (*3*), Ueno and Suzuki (*4*), and Dusenbury and Powell (*5*), to name only a selected few investigators widely spread in space and time.

There was not complete agreement, however, as some workers found the reaction more complex. Taylor (*6*) observed third-order kinetics and wrote for the reaction the rate equation

$$\text{velocity} \propto [\text{R—NH}_3^+][\text{HNO}_2][\text{NO}_2^-] \qquad (2)$$

Schmidt and Muhr (*7*) confused the situation further by finding two different rate laws, one in aqueous sulfuric acid,

$$\text{velocity} \propto [\text{Ar—NH}_2][\text{HNO}_2]^2 \qquad (3)$$

and a second in hydrochloric acid,

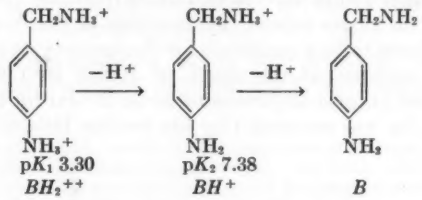
$$\text{velocity} \propto [\text{Ar—NH}_2](k_1[\text{HNO}_2]^2 + k_2[\text{HNO}_2][\text{H}_3\text{O}^+][\text{Cl}^-]) \qquad (4)$$

Until fairly recently, these anomalous results were ignored by many, and those textbooks which mentioned this aspect of the reaction followed Hantzsch, Morgan (*8*), and Saunders (*9*), and stated that diazotization is primarily a reaction between the amine salt and undissociated nitrous acid. When considered in the light of modern electronic theory, this seems hardly feasible, and recent investigation has shown conclusively that the reaction is between free base and a number of Lewis acids, of which one or more may be effective at any one time.

SALT OR FREE BASE?

There have been only two groups of workers who consistently maintained that the amine reacted as free base, the schools of Earl (*10*) and Kenner (*11*). Their arguments were relatively complex and difficult to follow. The simplest (and hence the most convincing) experimental evidence that such is the case lies in an overlooked and long-forgotten reaction discovered in 1889 by Salkowski (*12*). He found that when *p*-aminobenzylamine was diazotized in concentrated hydrochloric acid with one equivalent of sodium nitrite and the solution was then warmed, the product was *p*-hydroxybenzylamine, which was obtained in yields of not less than 87 per cent. Essentially the same reaction has been rediscovered recently by Kornblum and Iffland (*13*). By diazotizing *p*-aminobenzylamine with one equivalent of nitrite in hypophosphorous acid and then heating the solution, they found selective deamination occurred, giving benzylamine in 84 per cent yield. They also found that the aromatic amino group reacted readily at pH less than or equal to unity, whereas the aliphatic amino group was unaffected unless the pH was above three. In these observations lies the answer to the first difficulty.

Although the basic dissociation constants of *p*-aminobenzylamine have not yet been determined accurately, we can obtain a first approximation if we consider them to be of the same order of magnitude as those of benzylamine (K_b 2.4 × 10^{-5}) and of *p*-toluidine (K_b 2.0 × 10^{-9}). The corresponding pK's are 7.38 and 3.30.



The aliphatic amino group would certainly accept a proton first, and the subsequent inductive effect would weaken the aromatic amino group further, so that this approximation overestimates pK_1.

	pH 1	*pH 2*	*pH 3*	*pH 4*
B	1	100	6,700	167,000
BH^+	2,380,000	22,790,000	159,520,000	398,700,000
BH_2^{++}	476,190,000	455,780,000	319,040,000	79,700,000
Total	478,570,000	478,570,000	478,570,000	478,570,000

However, using these figures, a simple calculation shows that the relative amounts of the three species—free base, mono salt, and di salt—present at different pH are those given in the table. These figures are adjusted to same (arbitrary) number of aminobenzylamine molecules at each pH.

If the amine did react in the salt form, one would expect that all of the aliphatic amino groups would be affected at pH = 1, and most of the aromatic groups. The opposite has been found experimentally by independent workers: all of the aromatic groups are affected

and few of the aliphatic groups. Kornblum's observation that the aliphatic amino group is affected only at pH greater than three is readily understood from the table, which shows that free aliphatic amino groups do not appear in appreciable proportion until such a pH is reached. These figures demonstrate strikingly that diazotization must require the amino group to be present as free base.

We may conjecture here why the earlier workers fell into error over this point. While there is no direct evidence, one important fact which may have produced an unconscious bias toward the amine salt theory is that, whatever its mechanism, diazotization is a homogeneous reaction in solution, and since salts are more soluble than free bases, they are more suitable for practical diazotization. Even when the salt is not very soluble in water, this is still true: as the amine is consumed to give the much more soluble diazonium salt, more amine salt goes into solution and the reaction proceeds. Almost invariably the insoluble amines are weak bases, and the point that has been overlooked is that, as the salt goes into solution, it is immediately and extensively hydrolyzed to free base.

THE ACID REAGENT

Most of the workers in this field interpreted their results to mean that the undissociated nitrous acid molecule was the other effective reagent; the mechanism was considered to be aldol-type addition to the polarized nitrogen-oxygen double bond. That such additions do take place is shown by the many reactions of nitrosobenzene that resemble those of benzaldehyde, and by base-catalyzed reactions of nitrite esters that are similar to acetoacetic ester condensations.

If we return to the kinetic equations of Taylor, Schmidt, and others, it is apparent that the situation is not so simple as it might at first seem. These equations are complicated; they do not appear to be mutually consistent; and they cannot all be interpreted to mean that undissociated nitrous acid is the effective reagent. However, these equations were determined from experiments at a variety of acidities, and the confusion has recently been resolved by Hughes, Ingold, and co-workers (*14*, *15*).

These workers emphasize that when a reaction can be shown to be of second order, one is not justified in assuming it to be of first order with respect to each reagent; it may be of zero order with respect to one reagent and of second order with respect to the other. They demonstrated that diazotization changes from a third-order reaction at acidities above 0.05 *N* to second order at acidities below 0.002 *N*, and that this last reaction is of zero order with respect to amine and of second order with respect to nitrous acid.

$$[H^+] > 0.05\ N$$
$$\text{velocity} \propto [Ar{-}NH_2]^1[HNO_2]^2 \propto [Ar{-}NH_2]^1[N_2O_3]^1 \quad (5)$$

Rate-determining step:

$$Ar{-}NH_2 + N_2O_3 \rightarrow Ar{-}N_2^+ + H_2O + NO_2^-$$

$$[H^+] < 0.002\ N$$
$$\text{velocity} \propto [Ar{-}NH_2]^0[HNO_2]^2 \propto [Ar{-}NH_2]^0[N_2O_3]^1 \quad (6)$$

Rate-determining step:

$$2HNO_2 \rightarrow N_2O_3 + H_2O$$

This is interpreted to mean that the reaction is taking place by an aldol-type addition to the polarized nitrogen-oxygen double dond in dinitrogen trioxide. The change in reaction order results from the relative alteration in concentration of free base and N_2O_3 with pH and a corresponding change in the rate-determining step. At high acidities the availability of free base is rate-determining, whereas at low acidities the rate of formation of N_2O_3 controls. The situation is analogous to the more familiar case of a second-order reaction's becoming first order in the presence of a large excess of one of the reactants.

The rate equations of Taylor (equation 2) and of Schmidt and Muhr (equation 3) for reaction in sulfuric acid can be transposed immediately to this form. The equation of Schmidt and Muhr (equation 4) for reaction in hydrochloric acid indicates two simultaneous reactions, one with N_2O_3 and the other with nitrosyl chloride, NOCl, and is better written as shown:

$$\text{velocity} \propto [Ar{-}NH_2]([N_2O_3] + [NOCl]) \quad (7)$$

The results of the English school have been confirmed by the work of Shmid and Woppmann (*16*), who have developed a rather complicated rate equation which reduces to equation (5), (6), or (7), according to the experimental conditions.

We can now adopt a unified viewpoint for these reactions: They proceed by a "polar reaction" of two neutral but polarized molecules, an aldol-type addition of free base to the polarized nitrogen-oxygen double bond in one or more of the following molecules according to conditions.

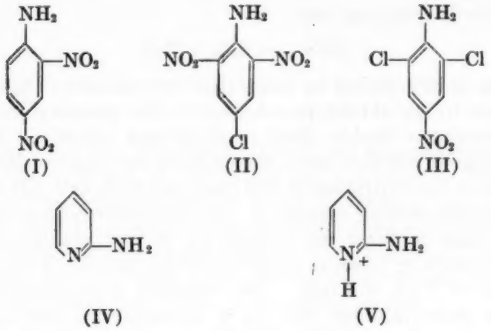
O=N—ONO
O=N—Cl
O=N—Br
(O=N—OH)

The nitrous acid molecule is shown in parentheses because Ingold's findings call for a re-examination of the results of Earl and his co-workers; it is clear from their publications that they did not consider the possibility of N_2O_3's being the effective reagent, and they did not check the constancy of the reaction order. Nitrosyl bromide is included; it would be expected to take part in reactions where the medium contains hydrobromic acid.

DIAZOTIZATION WITH NITROSYLSULFURIC ACID

Most diazotizations proceed according to the scheme above. However, there are some amines which cannot be diazotized under ordinary conditions in an aqueous medium, and another mechanism applies. Some such bases are shown below. (It should be noted that in

acid solution (IV) is almost entirely present as (V).) All of these amines are very weak bases, and we may



explain the failure of diazotization by normal methods by saying that the amino group does not have a sufficiently high electron density for the aldol-type addition to take place. Alternatively, we may say that the nitrogen-oxygen double bond in N_2O_3 is not polarized to the state where the nitrogen atom is electron-deficient enough. Therefore the conditions under which the reaction *does* succeed must provide a reagent in which the nitrogen atom is markedly electron-deficient. To paraphrase again, the effective reagent must be a powerful Lewis acid.

Such weak bases as those shown can be diazotized in nonaqueous media by "nitrosylsulfuric acid," which is now known to be nitrosonium hydrogen sulfate, $NO^+ HSO_4^-$. (The name "nitrosonium" was given by Ingold in analogy to the name "nitronium" for the NO_2^+ cation.) The existence of the nitrosonium ion was demonstrated originally by Hantzsch, and has since been confirmed (*17*). It is capable of normal electrophilic substitution reactions, and several nitrosations of aromatic rings undoubtedly proceed through its agency; diazotization by the nitrosonium ion may be formulated thus:

$$\mathrm{Ar{-}NH_2 + NO^+ \rightarrow Ar{-}NH{-}N{=}O + H^+}$$
$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N + OH^- \leftarrow Ar{-}N{=}N{-}OH}$$

Another ionic mechanism is possible, involving the hydrated nitrosonium ion, which may also be regarded as the product of the addition of a proton to the polarized double bond of undissociated nitrous acid:

$$\mathrm{H_2O + N{=}O^+ \rightleftarrows H{-}O{-}\overset{+}{N}{-}O{-}H \rightleftarrows H{-}O{-}N{=}O + H^+}$$

Ingold, *et al.* (*15*), have pointed out that the distinction between these two ions as reagents can be made only by very careful examination of the reaction kinetics.

Hodgson and Norris (*18*) have found difficulty in interpreting the mechanism of diazotization by nitrosylsulfuric acid in concentrated sulfuric acid, because in some cases diazotization does not occur until the reaction mixture is diluted with acetic or phosphoric acid. This difficulty is only superficial: in highly concentrated sulfuric acid the amine is present in salt form, and the nitrosonium ion does not react with the salt. When the solution is diluted with an acid weaker than sulfuric that is also a solvent for the amine, free base can be formed while the nitrosonium ion is still present and the reaction can proceed.

To summarize, diazotization involves always the free base and not the amine salt; it can be caused by several different reagents, but all of these can be accommodated within two mechanisms, one polar, the other ionic; and it is now possible to reconcile the apparent conflict in the various rate equations previously proposed for diazotization in aqueous solutions.

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CONTRIBUTIONS TO THERMODYNAMICS: THE ANOMALOUS HEAT OF VAPORIZATION OF HEPTANE

J. McQUIRG

A FEW years ago, some very precise data, painstakingly determined, were reported for the vapor pressures and boiling points of 52 highly purified hydrocarbons (*1*). From such data can be determined heats of vaporization. Assuming that the heat of vaporization may be represented by the relation

$$\Delta H = A' + B'T \qquad (1)$$

over a moderate temperature range, the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \qquad (2)$$

may be integrated, following the usual procedures, to obtain

$$\ln p = -A'/RT + (B'/R)\ln T + C' \qquad (3)$$

or

$$\log p = C - A/T + B\log T \qquad (4)$$

In order to determine whether such a simple equation would be satisfactorily precise over the entire ranges of pressure and temperature for which data are given, or whether it should be applied only to portions of the data (for each pure hydrocarbon), the equation was solved for the constants A, B, and C, for several groups of three selected points.

For heptane, it was found that values of $\Delta H/R$ calculated by extrapolating down with the equation based on points 1, 5, and 6 (Table 1 reproduces some of the data from reference (*1*) and Table 2 gives values of the constants derived) agreed fairly well with those calculated by extrapolating up with the equation based on points 14, 16, and 18. This indicated that the equation would be satisfactory.

But from the values of A and B, and the relation that

$$\Delta H/R = 2.3A + BT, \qquad (5)$$

the surprising fact is brought out that as the temperature increases, the heat of vaporization also increases, at least at temperatures above about 92°C. That is, B has a positive value. The fact that B increases with temperature is itself anomalous; that it becomes positive is quite startling. For normal liquids, the heat of vaporization decreases monotonously to zero at the critical point. So far, *n*-heptane is the only liquid tested that shows this anomalous increase of ΔH with T. (So far, *n*-heptane is the only liquid tested.) No adequate explanation of why the heat of vaporization should increase has yet been found, but it is certainly not a result of errors in neglecting the liquid volume and in assuming that the ideal gas laws are valid; the temperature is well below the critical, and the pressure below atmospheric.

EDITOR'S NOTE: This is another of "Dr. McQuirg's" papers intended to test our readers' ingenuity and insight. For a comment on this paper, turn to page 377.

TABLE 1
Some Vapor Pressure Data for *n*-Heptane

Point number	*Temp., °C.*	*Pressure, mm.*
1	98.781	768.08
2	98.217	755.31
3	97.710	744.11
4	97.160	732.12
5	92.060	627.98
6	84.832	500.75
14	42.597	103.66
16	35.993	77.28
18	29.648	57.42

It may be noted in this connection that heptane is the only straight-chain hydrocarbon that is found in certain pine trees instead of, or in addition to, the terpenes usually present, and it occurs in only two species: the Jeffrey pine (*Pinus jeffreyi*) and the digger pine (*P. sabiniana*) (*2, 3*). One would expect a C_5 or C_{10} hydrocarbon rather than heptane, since C_5 is the structural unit of the terpenes (*4, 5, 6, 7, 8*). It may be that the appearance of heptane is related to this thermodynamic peculiarity. The temperature at which this anomalous heat effect begins to be apparent is well above any that is likely to be encountered by a pine tree. Nevertheless there may be a catalytic phenomenon within the tree that takes advantage of this anomaly, with its consequent effect on the free energy of formation of this hydrocarbon from the precursor chemicals which in a pine tree normally give terpene compounds. The whole matter should be instigated further.

TABLE 2
Calculated Results for *n*-Heptane

Points used	*A*	*B*
1, 2, 3	−11,087.7	+79.7335
1, 3, 5	+ 855.568	+ 5.69779
1, 5, 6	+ 2355.13	− 3.67069
14, 16, 18	+ 2726.38	− 6.19821

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LANGUAGE AND SCIENCE

J. W. T. SPINKS
University of Saskatchewan, Saskatoon, Saskatchewan, Canada

AMONG the most striking developments of science in recent years have been the theory of relativity and the demonstration that matter and energy are interconvertible. These developments have led to a careful re-examination of the meaning of certain rather simple words, words such as length, time, matter, and energy, and this in turn has led to an increasing awareness of the importance of language in science.

While the interest of scientists in language is a relatively recent phenomenon, reflection on language itself is, of course, not new. In fact, reflection on language is one of the oldest and most constant preoccupations of the human mind. It appears that this preoccupation has been deepened at all critical points in human culture: at the time of the Greek sceptics, at the time of the medieval scholastics, at the time of the epistemologists of the eighteenth century, and finally now.

In the Upanishads we read: "If there were no speech, neither right nor wrong would be known, neither pleasant nor unpleasant, therefore, meditate on speech." Locke expresses the same thought: "When I first began this discourse on understanding, I had not the least thought that any consideration of words was necessary—but later—I found that unless their force and signification were well understood, there could be little said pertinently and clearly concerning knowledge."

In science also, language is of great importance since what science says can only be said in words, even though at times science has recourse to graphs and equations.

In considering what language is, we may say in the first instance that it is meaningful communication between man and man.

The question of using a language to express the meaningful rather than the unmeaningful, the true rather than the false, raises the question of linguistic validity. As to what is meant by the meaning of an assertion, Carnap says that it is the way in which "it may be verified," *i. e.*, the meaning is the verification. A consequence of this interpretation would be that all uses of language to which the question of truth and falsity is irrelevant are meaningless. While many would object that this interpretation is too rigid, it does approach the operational viewpoint, a viewpoint which has proved to be very useful in science and does not necessarily exclude other branches of knowledge such as art or poetry.

The modern attitude in science is that the true meaning of a term is to be found by observing what a man does with it, not what he says about it. Thus, scientists, by performing *operations*, which can be repeated by scientists, can reach agreement. All scientists know what is meant by the names oxygen and hydrogen and what is meant by the statement that "oxygen and hydrogen combine to form water," since each of the terms can be operationally defined.

Extending this approach to questions, for a question to have meaning it must be possible to find an operation by which an answer may be given to it. A great many questions become meaningless when analyzed by this approach, *e. g.*, May space be bounded? Look for the answer in experiment and not in your head. Similarly: May time have a beginning and an end? Are there facts of nature forever beyond our detection? Was there a time when matter did not exist?

The operational approach makes everything relative and also everything verifiable. If a concept is defined in terms of actual operations it will not be necessary continually to revise our attitude to nature.

Consider the word *length*. What is meant by the length of anything, for example, the edge of a post card? The card can, of course, be measured and it might come to, say, 5 inches. With a more accurate rule it might measure 5.1 inches, and still more accurately, 5.11 inches. Using a traveling microscope would add still more decimals, and using a traveling electron

microscope, still more decimals, but by this time the edge of the post card would be magnified so much that it would look quite irregular, and with a still further stage of magnification the observer would start to see the molecules constituting the edge of the card. Now these molecules are oscillating back and forth, and it becomes hard to say what constitutes the exact end of this post card. The observer might take the average position of the end atom, as it oscillated back and forth like the pendulum of a grandfather's clock, as constituting the edge of the card. However, at this point his physicist friend would tell him that there are electrons revolving about that end atom. The observer might then decide to take the extreme position of the electron in its orbit as being the "edge" of the post card.

But now he is caught because, in order to see the electron, he has to look at it with a light bundle or photon, and since he sees the electron, the light bundle must have collided with the electron, and the electron is therefore no longer where he thought he saw it. This means that the observer cannot possibly measure the length of the post card to any desired degree of accuracy. The same difficulty comes up any time an attempt is made to measure very small things exactly, and since this is the case, it would be better not to speak of lengths at all. Rather they should be called *lingths* or *langths* or *lungths*, anything which would avoid associating with the word the usual attributes of length.

Ordinarily the area of anything circular is given by $\pi r^2 = \pi \times \text{radius}^2$, but if the cross-sectional area of the nucleus of an atom is calculated in this way and then checked by bombarding the nucleus with neutrons, it is sometimes found that the calculations are out by a factor of 20,000. Now if $\pi \times \text{lingth}^2$ or $\pi \times \text{lungth}^2$ had been taken, an *irrea* or an *urrea* would have been obtained, certainly not an area, and the properties of this *irrea* would have been investigated operationally before anyone jumped to any rash conclusion about it.

Similar effects appear when measurements are extended to interstellar space where, for example, a star is said to be a certain number of light years away. Here the question of simultaneity comes in. Ordinarily there is no difficulty in deciding that a ruler has its two ends on the two points whose separation is required at the same time. However, it is quite otherwise in the case of interstellar distances, and an analysis of the question of simultaneity for such measurements led Einstein to his famous relativity theory with its concept of space-time. Quite obviously then, language is of considerable importance in science.

It would thus appear to be of particular importance that our concepts be so ordered that our present experiences do not place obstacles in the path of further inquiry. For example, Newton's definition of time, "Absolute, true and mathematical time, of itself and from its own nature, flows equably without regard to anything external, and by another name is called duration," shut the door on an examination of the concept of time, and it took an Einstein to force the door open. Quite obviously, then, in order to understand the world and our lives, a language must be used whose structure corresponds to physical structure.

One language that represents things rather well is mathematics, and a good understanding of it can be of help in grasping the relationship between things. By contrast, the language inherited from our primitive ancestors is such that it often provides separate terms for factors which are inseparable in fact and vice versa, *e. g.*, matter and energy, space and time. As a result, an attempt is made to split in our minds what is unsplittable in the real world. In optics the continual reference to light "waves" retarded the introduction of quantum theory, and even now speaking of wave and particle properties of photons and electrons introduces many difficulties. If a new experiment is not too far beyond the margin of known ground it can be explained with concepts derived from past experience; if not, an explanatory crisis develops, as in the case of the quantum theory and the theory of relativity. It is then advisable to adopt the operational approach, rather like a cautious kitten approaching a hot stove.

Many people still think that all experience must conform to familiar types, and of course language helps to confirm such tendencies. Even in quantum theory it is tempting to ask, why does the electron emit energy when it jumps? The talk of "probability" in quantum mechanics similarly proved irresistible to many of the philosophically minded and led some of them to indulge in wild speculations about casuality and free will. The difficulty is again mainly one of language. Probability was introduced into wave mechanics in an attempt to interpret the wave function ψ. "ψ^2 represents the probability of the electron's being found at that point at any instant." Operationally it is just something which is proportional to ψ^2 and at best is just in the category of an hypothesis. This is very different from probability in everyday affairs, *e. g.*, in throwing dice, where "probability" has an experimental meaning (statistics of large numbers of observable events).

Even in discussions of the scientific method some people have had difficulty in distinguishing "scientific" from "experimental," "laws" from "theories," "explanations" from "statements." For example, Boyle's law is considered as explaining his observations. This is understandable, as we commonly use the word "law" as the name for absolute truth, whatever that may be. The situation is not helped by using "law" in two fundamentally different ways, as in Newton's "law" of gravitation and Kepler's "laws." Kepler's "laws" were experimental. Newton showed that they were what one would expect if there were a force of attraction between bodies, without saying what this force is. His "laws" of motion are axiomatic. Maxwell's "laws" fall in the same category.

In talking about the operational approach, it should be noted that many constructs are very valuable; *e. g.*, the idea of an atom, the idea of stress in a beam or of an electric field. However, one should always be careful to distinguish between constructs and direct

data of experience. An electric field is determined by placing a charge there and measuring the force. The idea is an extremely valuable one, but many physicists go further and imagine the field as being real and that, furthermore, its existence involves the existence of a medium. The problem of the ether is thus largely a problem of language. An operational approach indicates that energy is possibly not entitled to the preeminent position that physical thought is inclined to give it. The interconversion of matter and energy is now well known, as is also Einstein's equation relating to this "interconversion." It would seem that Einstein could have simplified matters considerably by coining a word such as *mattergy*, matter and energy merely being different forms of mattergy, mattergy I and mattergy II. Their interconversion appears, then, as something to be expected and rather matter-of-fact, rather than a modern form of black magic!

In a few years' time our children will be verbally conditioned to such ideas and one can imagine coming up behind one of them and hearing him recite a little nursery rhyme on the way home from kindergarten:

> Oh, dear, what can the mattergy be,
> An A-bomb went off in my hair.

Actually, one does not need to go as far as mattergy to find linguistic difficulties in thermodynamics. If one thinks in thermodynamics of heat content as being literally "content of heat," one soon gets into difficulties. These are avoided (at least partly) by talking about enthalpy and noting that enthalpy $H = E + PV$. The pressure, P, and volume, V, are operationally well understood, and some people claim to know what the internal energy, E, is. However, when E is examined operationally, it is found that it is never measured absolutely, but that only changes in E, ΔE, are measured (equals $q - w$, which can be measured). So an operational point of view would talk about "changes in energy" going past the boundaries of a system. The first law of thermodynamics then reduces to saying that as "change in energy" crosses the boundary surface, the increase inside equals the amount which crosses, *i. e.*, it is conserved. Instead of stating the first law of thermodynamics as, "The energy of the world remains constant," which is a theory and not a law, we could state it as a law: "In any change, chenergy (change in energy) is conserved." This is an experimental law and could be brought up to date by stating it in the form, "In any change, chmattergy is conserved." (Chmattergy equals change in mattergy.) One difficulty about speaking of energy is that there is a tendency to extend the verbalization and think of energy as analogous to matter. It is possible to detect changes in mass passing a bounding surface, *e. g.*, adding a pound of iron. It has operational meaning to say, "There is so much matter in this enclosure, say two pounds of iron," but the same is not true for energy.

Another language difficulty arises in the use of the word *isotope*. Isotopes have the same atomic number but different atomic masses, and it is, therefore, correct to speak of U^{238} and U^{235} as isotopes of U. It is, however, not correct to speak of a table of isotopes any more than it is to call a telephone directory a table of brothers and sisters. Such a table should be called a table of nuclides or, according to a recent suggestion, a table of monobars. (A nuclide or monobar is a species of atom characterized by a definite type of nucleus, *i. e.*, one having a definite number of protons and neutrons.)

Everyone is familiar with the so-called "normal" curve. Many attempts have been made to establish a law of nature known as "the normal law of errors," the name of which implies that errors ought always to be distributed in this way. The use of "normal" implies more than is justified by the facts, the adjective *normal* being one which is established by custom and which provides a convenient label for a distribution of this type. To quote Poincaré:

> Everyone believes in the Gaussian error curve because the mathematicians think that it is a natural law and the scientists think that it has been proven mathematically.

Science has been defined by some as any verifiable and communicable knowledge. Others seek to define it in terms of method, the method of science being that of framing wider and wider generalizations based upon observation and experiment. There is no doubt that since the days of Galileo there has been an attempt to bring all science into a mathematical form. The ideals of a scientific language are definiteness and exactness. In fact, some have claimed that "science is language well made," and this closely parallels the idea of science as being "organized common sense." Its language would then be, in principle, the language of common sense. Unfortunately, recent developments in quantum mechanics get so far from the usual idea of common sense that even a person like H. G. Wells exclaims that "in the heights or depths of modern physics" his mind "sinks down exhausted!"

Physical science began with a literal or copy theory of concepts. With Galileo, secondary qualities were stripped off, leaving only the primary qualities of extension and motion. Even in the nineteenth century the understanding of a physical happening was thought to be equivalent to the ability to make a mechanical model or physical picture of it. With electrodynamics, the copy theory was abandoned.

The ideal of science was no longer to picture but to predict.

The function of the scientific concept is now to symbolize reality and not to picture it, mathematics supplying the fundamental symbolism, *e. g.*, the concept of light progresses through Newton's corpuscles, Huygens' waves and Planck's quanta to a wave-mechanical ψ (!). To speak of wave and corpuscle properties then becomes nonsense.

Of course not all constructs of modern physics are of this type. In fact, one physicist has distinguished three classes of constructs or symbols: (*a*) the sensible, *e. g.*,

physical models; (*b*) pseudo-sensible, *e. g.*, atoms and electrons; (*c*) the abstract or wholly insensible, *e. g.*, quantum mechanical in which the electron and any other physical system is replaced by an abstract construct.

Before leaving the question of language, one should of course point out that in poetry, for example, certain aspects of reality which are perhaps otherwise inexplicable are sometimes expressed best by deviations from the real—such as T. S. Eliot's:

> They are rattling breakfast plates in basement kitchens
> And along the trampled edges of the street
> I am aware of the *damp souls* of the housemaids
> Sprouting despondently at area gates.

While this verges on the grotesque, it is revelatory to an extraordinary degree.

While the exact significance of what poets say may be questioned, there is no doubt that poetic and artistic symbols do awaken within us powerful feelings.

To quote another writer:

> Art in all its forms, asserts the reality of the experienced qualities of things. The poet hears the rippling brook, and unlike the physicist, he does not abstract the atoms and sound waves and forms of running water. . . . That which the poet catches and the physicist misses is the bare indeterminate experienced quality which the psychical contributes, and this has its roots neither in observed nature nor in man, but in the ultimate atomic elements out of which both are constituted.

Actually, that which he catches is not physics but metaphysics!

Naturally one does not wish to dispense with poetry, fiction, fantasy, or emotions, since life would indeed be duller without them.

But more and more in science the philosophy of the operational approach should be adopted, for even in science words are not always what they seem and an eloquent but wrong use of words has often "lent an air of verisimilitude to an otherwise improbable hypothesis."

LENSLESS COPYING WITH SENSITIZED PAPERS[1]

FRANK E. SMITH
General Motors Photographic, Detroit, Michigan

MANY of the newly available sensitive materials have added impetus to the development and use of lensless copying methods. In fact, today so many products are being offered by various manufacturers that desirable clarification can be obtained only by an understanding of the two basic reproduction procedures and the principal types of sensitive goods employed.

In all lensless copying procedures the common characteristic is the necessity for having the original document and the sensitive means in close physical contact when the printing exposure is made. The two basic methods employed are the print-through and reflex procedures, the first utilizing light transmitted through the original document and the second utilizing light reflected by the document. Three basic sensitive material types are employed: diazo, iron, and silver-sensitized paper, film, and related supports.

In the simpler type of lensless copying an original document capable of transmitting light is required. Important factors are the homogeneity of the base, the density of the sheet, and the opacity of the image to be reproduced; but the fundamental characteristic of the procedure is the translucent or transparent original. Printing is effected by placing the translucent original in contact with the sensitized material and directing light through the original to the sensitive surface. The document image areas possess density which absorbs light and thus a varying photochemical effect is obtained in the sensitized surface. The latent image is rendered visible by processing means associated with the particular type of sensitized material employed.

Diazo sensitized papers are often used in lensless copying for low cost, speed, and positive color images, but a translucent original usually is essential. Among the many manufacturers of diazo products, the Ozalid Division of GAF have seen their trade name, Ozalid, become almost a generic name for diazo reproductions.

Diazo papers and other diazo products are coated

[1] Presented as part of a Symposium on "Equipment for the Preparation, Reproduction, and Utilization of Technical Information," at the 124th Meeting of the American Chemical Society, Chicago, September 9, 1953.

with a light-sensitive diazo compound which may be destroyed by light. In the dry diazo papers the diazo compound and the coupler are coated in an acid state upon the base. After light exposure, the remaining diazo compound and the coupler react to form an azo dye when the paper is subjected to an alkaline atmosphere in the ammonia-fume development section of the machine. The wet diazo paper is coated with the diazo compound alone. Following light exposure, the paper with the remaining diazo compound is roller-moistened with an alkaline coupler and an azo dye image is formed. Exposure normally is effected on a continuous machine by which the document is conveyed around an interior-illuminated glass cylinder, the document in contact with a sheet or roll of sensitized paper. Since the image formed on any diazo print is the function of the undestroyed diazo compound, the area protected by the image of the original document, a positive color reproduction, like in tone to the original, is obtained. This characteristic, its relative low cost, and relative dimensional stability have been important to its continuing acceptance and growth.

Iron-sensitized papers, the ordinary blueprint, yield low-cost volume copies of translucent originals. With the blueprint method old and well established, there are many sensitized paper sources; Paragon-Revolute and C. F. Pease are among the important equipment manufacturers.

Suitable roll paper is coated with ferric salts which are changed by exposure to light and will react to form the well known blue precipitate characteristic of blueprints. Printing usually is effected on continuous machines by feeding the document around an illuminated glass cylinder in contact with sensitized roll paper. Processing is carried through several wet stages on the machine and only continuous roll lengths of sensitized paper can be utilized. Reproduction is opposite in tone to the original document; a dark original line reproduces as white or light in blueprinting. Low costs are obtained on volume production.

Silver-sensitized papers are available from many sources in a wide range of speeds and types, and find considerable use in lensless copying. The usual equipment furnished by such manufacturers as Remington Rand or Hunter Photocopyist is quite simple and inexpensive; manual handling ordinarily is employed. Paper, or other base, is coated with a light-sensitive silver halide emulsion. A translucent original is placed on a box-like printing frame, covered with a sheet of silver-sensitized paper, and light is directed through the original document to the sensitive paper, forming a latent image in the silver-sensitive surface. A photographic developer solution reduces the exposed latent image to visible metallic silver. The unexposed undeveloped silver halide is dissolved with hypo; and for permanence, all soluble materials are washed away. Most silver-sensitive materials are coated on high-grade base and are manufactured to higher standards than other paper types, which with proper manipulation will permit a high quality of reproduction to be obtained with silver materials.

Normal reproduction with silver-sensitive materials is opposite in tone to the original document. Thus negative tone prints result as the first generation duplicate of the conventional translucent original. Where negative tone reproduction is undesirable, a print may be made of the first negative copy for a positive tone reproduction.

A specialized type of silver-sensitized paper and film utilizing the Herschel effect is available from Eastman Kodak Company and will yield a positive tone reproduction from a positive tone original. Known as Kodagraph Autopositive, handling procedure is quite normal except that longer wave-length yellow or orange illumination is essential for the original exposure. Results are of excellent quality.

The inconvenience of wet handling of photographic papers has encouraged the development of devices for the "dry" processing of silver-sensitized materials, specialized silver coatings originated in Europe. On a device such as the Remington Rand Transcopy Duplex, and similar equipment from other sources, such as Copease and Apeco, a translucent original may be exposed onto sensitive paper, after which the exposed paper is mechanically conveyed into the photographic developer and almost simultaneously squeegeed in face contact with a sheet of special receiving paper. The diffusion of the unreduced silver halide of the exposed sheet into the receiving paper and its immediate reduction in the receiving sheet result in a positive tone reproduction on the receiving paper sheet. The convenience and speed of reproduction are important advantages.

The Eastman Kodak Verifax unit is another ingenious "dry" procedure recently available employing a different silver-sensitive approach. Exposure may be effected in the conventional manner; but the silver-sensitized paper also incorporates a tanning developing agent and other materials. The processing solution produces a tanned silver negative image and a general dark dye deposit throughout the sheet. Thus an untanned dyed positive image is obtained on the sheet. When the negative sheet is conveniently squeegeed to an ordinary sheet of receiving paper, some part of the soft dyed positive image is transferred to the receiving sheet. Although each succeeding print squeegeed from such a negative becomes lighter, several legible positive reproductions can be obtained by successively transferring the negative sheet to receiving paper.

Heat-sensitive papers are one of the newest additions to the large group of lensless copying procedures. Thermofax, offered by Minnesota Mining, is a method employing their material, a printing unit including a frame and a traversing source of heat and light. A translucent original may be placed in the frame and covered with a sheet of heat-sensitive paper, consisting of a front light-colored and a rear dark-colored waxlike coating on a lightweight paper base. When traversed with the light source, the dark image areas of the origi-

nal document absorb heat and melt the wax coating of the sensitive sheet to yield a visible image instantly.

While original documents can be prepared on a translucent base and reproduction thus facilitated, many originals exist on an opaque base or bear dissimilar images upon the front and back of the sheet. Obviously such documents cannot be copied by the simpler print-through technique. Some sensitive goods can be manipulated to produce images from the light reflected from such opaque or double-faced documents. Usually a primary requirement is that the sensitive material possess high contrast, the ability to reproduce small differences in light intensity as large differences in image density. For exposure the original document and sensitive goods are placed in face contact; but the light is directed through the back of the sensitized sheet. The illumination transmitted by the sensitized sheet then strikes the surface of the original document. The darker image areas of the original absorb some of the incident illumination, but the lighter background areas reflect back to the sensitized surface. If the sensitive sheet possesses desirable dispersion and reflection characteristics, additional inter-reflection is set up. In such manner the sensitized sheet receives differential exposure from the illumination reflected from the original document. Although the sensitized material has received some exposure from the original illumination transmitted through its base, the desired high contrast of the sensitive goods will exaggerate the relative light values and yield a practical negative from the reflected illumination. This procedure is well known as reflex copying and has found a wide measure of usage and acceptance. The first reflex print is negative in both tone and reading. Consequently, it must in turn be reproduced for a positive-tone right-reading print.

Reflex technique has some advantage, other than its obvious ability to copy opaque or double imaged documents, in that the reflection density variance of assorted documents usually is less than the variance in transmission density of similar originals, thus reducing one process variable.

Diazo materials usually do not yield satisfactory reflex images since most of the light-sensitive diazo compound is destroyed by the transmitted illumination. One diazo product, Bruning Reflex Film, is available carrying a fine strippable opaque screen which protects most of the diazo coating from the rear-transmitted illumination, permitting it to be exposed from the front-reflected light, by which good diazo reflex prints can be obtained. Reflex images of low quality on unscreened film can be obtained by filtering the exposing illumination to longer wave lengths than are normally used in diazo printing.

Iron-sensitized materials do not possess suitable characteristics for the reflex copy of opaque and other originals.

Silver-sensitized materials are extensively used in reflex lensless copying. Photographic emulsion coatings possessing high contrast can be produced, and such materials can yield excellent reflex results. Darkroom or white light handling silver-sensitized reflex papers are exposed to an original document often using yellow or longer wave-length illumination. After exposure in a regular printing frame, a mechanical printer, or the portable Ludwig Contoura, the paper is processed in normal photographic solutions to obtain a negative-tone negative-reading reproduction. Often positive prints then are obtained on silver-sensitized paper, although the reflex negative can be used as an intermediate for reproduction on any type of sensitized paper.

The Kodak Autopositive type of sensitive material, handled in normal reflex fashion, will yield positive color negative-reading prints which are good intermediates for subsequent diazo reproduction.

Both types of the "dry" photographic processes, involving the chemical and the Kodak physical transfer methods, produce acceptable reflex copies. The consistency of the light transmission density of the silver-sensitized paper base compared to the varying transmission qualities of different documents when reproduced by the print-through method actually represents a manipulation advantage for the reflex procedure.

Minnesota Mining Thermofax heat-sensitive papers may be successfully employed in reflex printing. Printing is so arranged that the sensitive paper transmits the energy first, before the image areas of the original absorb the energy and melt the adjacent coating.

While not precisely classified as either a print-through or reflex procedure, another method should be given consideration. The Times Facsimile Stenafax and the Winchester Industries Facsimile units enable a document of limited size to be affixed to a rotating cylinder where it is minutely scanned by a photocell pickup. The signal from the pickup actuates a stylus mounted before a similarly rotating cylinder bearing a receiving paper or stencil. Scanning time for a letter-size document is several minutes, and results are of a practical quality.

It can be recognized, therefore, that although there are a host of lensless copying materials and apparent processes, there are but two basic procedures, the print-through and reflex methods, and a few principal sensitized material types.

THE PERMEABILITY METHOD FOR THE MEASUREMENT OF SURFACE AREAS OF FINE POWDERS

J. A. ALLEN and C. J. HAIGH
The University of Tasmania, Tasmania, Australia

ALTHOUGH the measurement of the surface area or particle size of a moderately fine powder is frequently an important procedure in industrial laboratories, it is seldom included in laboratory courses in physical chemistry in universities and technical colleges. Of the large number of methods available (*1*) some form of the permeability method based on the measurement of the rate of flow of air or other suitable fluid through a plug of the powder is, perhaps, the one most frequently employed industrially. A commercially made apparatus in common use, although very convenient for routine work in that the desired answer is given directly, is unsatisfactory for teaching purposes, since its operation requires no knowledge of the theory on which the measurement depends.

In this contribution the theoretical background of the permeability method is briefly reviewed. A simple, inexpensive apparatus which requires a minimum of constructional skill, but which has proved its reliability, is described. A useful comparison is made between the results of a large number of measurements on nickel oxalate precipitates carried out with this apparatus and by means of a simple optical method. Some important limitations for very fine powders are indicated.

THEORY AND APPARATUS

Permeability methods are based on the measurement of the rate of flow of a gas or other suitable fluid through a plug of the powder being investigated. The fundamental relationship is contained in Darcy's equation (*2*),

$$Q = \frac{K_1 A \Delta P}{L} \tag{1}$$

where Q = volume rate of flow through the plug; A = area of the plug; L = length of the plug; ΔP = pressure drop across the plug; and K_1 = constant.

The original equation was deduced from measurements of the flow of water through porous beds of sand, but has been extended and treated theoretically, notably by Kozeny (*3*). He considered the flow of a fluid through a porous medium as equivalent to that through a group of parallel channels, for which the total internal surface and the total internal volume were equal, respectively, to the particle surface and pore volume in the medium. Kozeny's equation is

$$U = \frac{\Delta P g \epsilon^3}{K L \eta S^2} \tag{2}$$

where $U = Q/A$ = linear rate of flow through the bed; ΔP = pressure drop across the bed; g = acceleration due to gravity; S = surface area of particles in unit volume of the bed; K = constant, which by experiment is equal to 5.0; η = viscosity of the fluid; ϵ = porosity of the bed, defined as the total volume of voids divided by the gross volume of the bed.

Mathematically the porosity function is defined by the equation,

$$\epsilon = 1 - \frac{W}{AL\rho} \tag{3}$$

where W = weight of material in the bed; ρ = density (bulk) of the material comprising the bed; and A and L are as defined for equation (1).

All permeability methods involve some modified form of equation (2). There are two general methods of utilizing the Kozeny equation. In the first, used by Carman (*4*) and others (*5*, *6*), a fluid, usually a gas, is driven through the powder bed under a constant pressure head. The appropriate equation is

$$S_w = \frac{S_o}{\rho} = \frac{14}{\rho}\left(\frac{A \Delta P}{QL\eta} \frac{\epsilon^3}{(1-\epsilon)^2}\right)^{1/2} \tag{4}$$

where S_w = surface area in cm.^{2} per g.; S_o = specific surface of the particles, *i.e.*, the total surface divided by the total volume; Q = rate of flow in ml. per sec.; and the other quantities are as previously defined.

A second method employs a steadily diminishing pressure head, measurements being made simultaneously of the pressure drop across the bed and the rate of flow. While this requires a more complex modified Carman equation, it permits the use of a very simple apparatus suitable for student use. A sketch of the apparatus based on the design of Rigden (*7*) is shown in Figure 1.

The two ends of the U-tube of uniform bore, 2 cm., and about 30 cm. in length, half-filled with ethylene glycol, are each sealed to an oblique-bore 2-way stopcock. One bore from each stopcock is connected to a demountable glass tube in which the powder plug is packed. The second bore from each of the two stopcocks is open to the atmosphere via a silica-gel drying tube. The whole apparatus is mounted on a wooden stand which carries a graph paper scale behind the U-tube. The liquid in the U-tube serves the triple purpose of providing the means of driving the air through the bed, of indicating the pressure drop across the bed at any instant, and of measuring the rate of flow.

Rigden modified Carman's equation for an apparatus of this kind and obtained the following expression:

$$S_w = \left(\frac{2Agdt\,\epsilon^3}{K(1-\epsilon)^2\eta\rho^2 aL[\log_e h_1/h_2]}\right)^{1/2} \quad (5)$$

where d = density of the liquid in the U-tube; a = area of cross section of the U-tube; K = constant = 5.0; t = time in seconds for the liquid in the U-tube to fall between two marks, h_1 and h_2 cm., respectively, above the equilibrium value. Other symbols have the same meaning as before. This equation may be simplified when the constants of the apparatus are known, *viz.*,

$$S_w^2 = kt\epsilon^3/(1-\epsilon)^2\rho^2 L \quad (6)$$

where

$$k = 2Agd/K\eta a \log_e h_1/h_2 \quad (7)$$

For routine work on a single material a standard weight of which can be compacted to a fixed depth the expression reduces to

$$S_w = k_1 t^{1/2} \quad (8)$$

where k_1 is a constant. In general, it is preferable for instructional purposes to use a different weight of powder for each determination and to study changes in the results arising from this and from the use of different values of the porosity function.

PREPARATION OF THE PLUGS

The glass packing tube of uniform bore (1.55 cm.) is snugly fitted with two perforated brass discs, 0.6 cm. in thickness, through which as many as possible $^1/_{32}$-inch holes have been drilled. The central hole is tapped to take a screwed rod by means of which the disc is readily handled. One disc rests on a slight concentric indentation run in on the glass tube with a small sharp flame and is fixed in place with picein wax. A filter paper disc (Whatman No. 1) is placed on the fixed disc; a weighed amount of powder, 6 ± 2 g. in our experiments with nickel oxalate, is added to the tube a portion at a time, the tube being gently tapped after each addition. When all the powder has been added a second filter paper disc is inserted and the second brass disc temporarily attached to the screwed rod is used to compress the powder. The ideal bed should have an even packing and the most consistent results are obtained with beds of porosity ϵ = 0.4–0.5.

PROCEDURE

When the plug has been prepared and the apparatus assembled the liquid in the U-tube is raised in one limb by applying a vacuum to that limb, the other limb being open to the atmosphere. The two stopcocks are then adjusted so that the U-tube limbs are connected via the powder bed. The time taken for the liquid to fall between two marks, h_1 and h_2 cm., respectively, above the equilibrium value, is noted. The height of the bed is readily measured by a finely divided scale held against the packing tube. It is convenient to measure the distance between the outer edges of the brass discs and to correct for the two thicknesses of brass and filter paper. The calculation of the results is illustrated below:

a = area of cross section of U-tube = 3.142 cm.^{2}
A = area of cross section of bed = 1.88 cm.^{2}
ρ = density of nickel oxalate dihydrate = 2.235 g. per cm.^{3}
η = viscosity of air = 180.8 × 10^{-6} poise
Equilibrium level in U-tube = 11.92 cm. on scale
h_1 = 9.92 cm.; h_2 = 3.92 cm.

With these figures the expression for S_w reduces to

$$S_w = \left(\frac{\epsilon^3 t}{(1-\epsilon)^2 L}\, 3.122 \times 10^8\right)^{1/2} \quad (6)$$

and

$$\epsilon = 1 - W/4.202L \quad (7)$$

Measurements of W, L, and t enable S_w to be evaluated.

OPTICAL METHOD

As most teaching laboratories have available a photoelectric absorptiometer it is convenient to compare measurements of surface areas by the above method with those obtainable with the absorptiometer using the following method: When an opaque powder is dispersed in a suitable liquid and a beam of light passed through the suspension, the amount of light cut off is related to

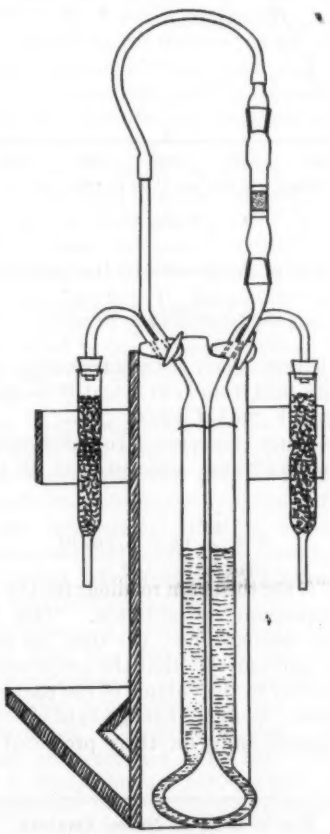

Figure 1

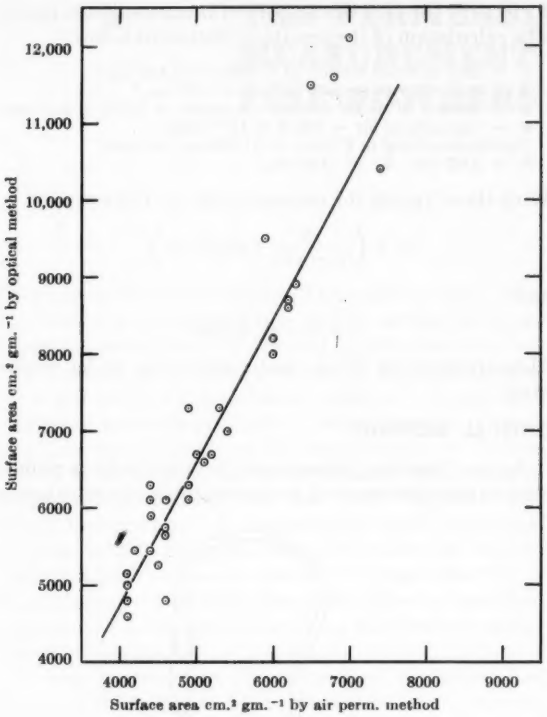

Figure 2

the surface area of the powder by the relation

$$S = \frac{4V(\log_e I_o - \log_e I_s)}{WL} \qquad (8)$$

where L = length in cm. of the suspension in which the light intensity falls from I_o to I_s and W = weight of the powder in g. in V cm.³ of liquid.

Since the drum readings of the absorptiometer are usually on a logarithmic scale to base 10, the formula simplifies to

$$S = \frac{4V}{WL}(\theta_o - \theta_s)\log_e 10 \qquad (9)$$

where θ_o and θ_s are the drum readings for the clear liquid and the suspension, respectively. This formula is based on two assumptions: (1) that the particles are spherical, or alternatively that the projected area bears the same relation to the volume of the particle as in the case of a sphere; and (2) that the light obscured by the particles depends only on their projected areas. It should also be noted that the Lambert-Beer law of light extinction fails when the particle diameter becomes comparable with the wave length of light. This limitation is not serious for powders in which there is little material below 2.5 μ in diameter. The formula also fails to take into account any settling of the suspended material so that if the powder contains particles over a considerable size range, errors are to be expected.

Results obtained with this optical method and those derived from sedimentation data have been shown to afford different figures (*8*), but a correlation exists and hence the calibration of one method in terms of the other is possible. A similar comparison of measurements by the permeability and optical methods for nickel oxalate precipitates is shown in Figure 2. It is clear that there is a satisfactory correlation over a considerable area range, the optical measurements giving results higher by a factor of ~1.8. This factor is of the same order as that given by Sharratt, *et al.* (*8*) for a comparison between the optical and sedimentation methods for opaque materials. Agreement between any of these methods cannot, of course, be expected since each is based on a different set of assumptions.

Precipitates of Nickel Oxalate

Group	*No. of powders*	*Range, cm.² per g.*	*Mean limits, cm.² per g.*
I	28	4000–6000	± 80
		6000–8000	±100
		8000–12,000	±600
II	24	4000–6000	± 60
		6000–8000	± 65

ACCURACY AND LIMITATIONS OF PERMEABILITY METHOD

The reproducibility of the results can be seen from the data on precipitates of nickel oxalate given in the table. Precipitates in Group I were prepared at 20°C. and in Group II at 40°C. All powders were measured in quadruplicate with different amounts of material in the range 6 ± 2 g. compressed to different porosities in the range 0.4–0.6. Microscopic examination showed a greater variation in particle size in Group I and this probably accounts for the somewhat larger limits in this group.

For certain types of routine work on one substance it is often convenient to use a fixed amount of material compressed to a definite porosity. Under these circumstances the reproducibility is very high. Finally, we note that for powders of surface area greater than 12,000 cm.² per g. the errors become gross. This is to be expected since the simple theory of the method no longer holds for particles of this size and appropriate slip correction factors have to be applied. These have been discussed in detail by Carman and Malherbe (*9*).

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GEORG WITTIG

RALPH E. OESPER
University of Cincinnati, Cincinnati, Ohio

SMALL incidents sometimes have important consequences. When Georg Wittig was in the later years of the elementary school, a copy of "Chemische Experimente aus dem Alltag" (chemical experiments from everyday life) came into his hands. The first experiment in this little manual, namely the fact that red-cabbage water turns green with soda and that the red color is restored by vinegar, impressed him so much that he could never again tear himself loose from the fascinations of chemistry. The pleasure of making observations and the joy of chemical manipulations became the foundation of his future research activities. This process of developing into a scientist was interrupted by military service and imprisonment (1916–19) but it was never subjugated by other distractions or interests.

Georg (Friedrich Karl) Wittig was born at Berlin on June 16, 1897. His father was an artist; his mother was very devoted to music. Consequently, his youth was spent in a cultural atmosphere. The German youth movement "Wandervögel" (migratory birds) played a significant part in his education; it awakened in him an appreciation of nature and taught him the value of true comradeship. The combination of humanistic training, art, and love of nature was responsible in great measure for the shaping of his future career.

After he finished the course at the humanistic Gymnasium at Cassel in 1916 his education was interrupted by the war. In 1920 he eagerly began his professional training at the University of Marburg. Since three other members of the family were also in school, his financial resources were skimpy. He devoted himself solely to science and found his recreation at the piano in the evenings. His principal teacher, Karl von Auwers (1863–1939),[1] under whom he took his doctorate in 1923, was reserved, strict, and just. He taught his students to work cleanly. While Wittig was serving as assistant in the inorganic division, von Auwers encouraged him to prepare himself for a Privatdozentship. The habilitation was achieved in 1926; the underlying research was in a purely preparative field and dealt with chromone and cumarin syntheses. Many suggestions came from Wittig's close friend, the brilliant thinker and enthusiastic experimenter, K. Ziegler[2] and also from the Göttingen friend, W. Hückel,[3] whose comprehensive information and critical attitude were offered to Wittig during their excursions on foot. H. Meerwein, who succeeded von Auwers at Marburg, made Wittig enthusiastic about his ideas, which came into their own somewhat later and which also had an effect on Wittig's investigations. These contacts with the theoretical side of chemistry resulted in Wittig's excellent "Stereochemie" (388 pages), which was published in 1930.

In 1932 Wittig went to Braunschweig, where he was Division Head at the Technische Hochschule, and only then did he secure enough co-workers to realize his ideas. He soon became a close friend of the head of the Institut, K. Fries, a particularly gifted experimenter. At this time, the political unrest was reaching even into the institutions of higher learning and many of the faculty members were greatly concerned by the possible implications of the new state doctrines. When Wittig was called to the University of Freiburg in 1937 as associate professor of organic chemistry, he found that the political impacts were much less noticeable there than in some of the other schools. Here his scientific horizon was greatly widened by the close contact with macromolecular chemistry, a field which the head of the Institut, H. Staudinger[4] had founded and was developing to a considerable extent. In 1944 Wittig was called to his present position, head of the department and ordinary professor at the University of Tübingen.

From the very beginning of his research career Wittig has made it a cardinal principle to experiment and to experiment again and again, with no regard to present conditions, technical applicability, or possible outside recognition. Results awakened ideas which at times led him astray, but sometimes they resulted in further advances. This interplay between experiment and imagination led him to an involuntary but logical sequence in his research activities.

He began with the cleavage of the chromones to dicarbonyl compounds by means of alcoholate. In one case he succeeded in preparing the four possible stereochemical dioximes. The proof of their configurations brought him into contact with the interesting discovery by J. Meisenheimer (1876–1935), who carried out an independent proof of the configuration by means of the ozonide splitting of triphenyl isoxazole. Since at that time Wittig thought it possible that the ring-opening of the energy-rich ozonide would lead to the flipping of the hydroxyl group to the opposite side,

[1] For biographical details see MEERWEIN, H., *Ber.*, **72A**, 111–21 (1939); THORPE, J., *Chem. Ind.*, **17**, 838–40 (1939).
[2] See J. CHEM. EDUC., **25**, 510 (1948).
[3] *Ibid.*, **27**, 625 (1950).
[4] Staudinger was awarded the Nobel Prize for this contribution; see the numerous appreciations published in 1953; also J. CHEM. EDUC., **16**, 1 (1939).

he studied the ozonization of isoxazoles in additional instances but found no confirmation of his ideas. They led him, however, to the new idea of investigating the tension in those rings which exhibit a loosening due to radical-forming substituents on a C-C bond. This connection between ring tension and radical formation led to a series of studies, which spread in a variety of directions. During the synthesis of ω,ω' tetraphenyl-enepolyenes with their somewhat striking characteristics, there arose the problem of valence tautomerism, whose limiting validity had been outlined by Wittig as early as 1930. The new investigation led him to the development of new methods of obtaining polyene chains, a problem that is still claiming part of his attention.

This work also took him into the chemistry of the lithium-organo compounds. In conformity with the scheme

$$RO_2C—CO_2R \rightarrow HO(C_6H_5)_2C—C(C_6H_5)_2OH$$

the pertinent glycols need to be prepared if polyenes are to be obtained from dicarboxylic esters. Although the reaction of the diesters with phenyl magnesium bromide gave but small yields of the glycols, the reaction proceeded much better when phenyl-lithium was employed, a reagent that had recently been made readily available through the work of K. Ziegler. When this reagent was replaced by *p*-anisyl-lithium, however, prepared from lithium and *p*-anisyl bromide, unravelable mixtures again resulted. A surprising product was obtained when benzophenone was allowed to react with the organometallic solution, namely, bromo-anisyl-diphenyl carbinol instead of the expected *p*-anisyl-diphenyl carbinol. This discovery ushered in a series of extended researches dealing with the metallation of phenol ethers; they led to the phenomenon of the halogen-lithium exchange reactions and to rearrangements within the molecule. In this way there came into being an organic aniono chemistry, whose development is at present the chief aim of Wittig's researches. He is also working on the problems of autoxidation and its inhibition and on various topics in radical- and stereochemistry.

The working out of the research plans of a university professor usually requires the collaboration of a staff of co-workers recruited from doctoral candidates and research fellows. The relative lateness of Wittig's maturing process and the external conditions of the country had the result of making him 35 before he could unfold in the scientific sense. As a rule, about a dozen young men are working with him, a number which in his opinion is optimal for the greatest efficiency of the teacher and the maximum benefit to the student. He found that the veterans who returned to the universities after the political collapse of Germany were outstanding, since the resolve to study under the most difficult conditions is equivalent to a careful screening. He feels that special thanks are due to such men when their scientific collaboration led to results which gained respectful recognition in the chemical world.

Professor Wittig refused a call to head the Institut at the University of Freiburg in 1950 because the building still needed to be reconstructed. In 1953 he was elected corresponding member of the Bavarian Academy of Sciences, and in this same year the Gesellschaft Deutscher Chemiker awarded him its Adolf von Baeyer memorial medal.

ERRATUM

We are indebted to Professor John O. Edwards of Brown University for calling attention to an error in the paper, "Isomers of octahedral complexes with nonbranching ligands," in This Journal, **31**, 176 (1954). In the case of a complex with three of the same bidentate ligands with nonequivalent groups, $(AB)_3$, there are two structures, both optically active, possible. They would be, in the nomenclature used, **fac-A** and **mer-A.**

SOME ASPECTS OF ISOTOPIC EXCHANGE

ROLFE H. HERBER
Massachusetts Institute of Technology,
Cambridge, Massachusetts

DURING the war the necessity for separating large amounts of a given element into fractions enriched in one or another of its stable isotopes first served to focus the attention of a large number of chemists on the field of isotopic exchange. The increasing availability of radioactive isotopes of most of the common elements, and of rugged, stable, and relatively foolproof instruments for radioassay, in recent years has widened the opportunities for research in the field of isotopic exchange, and has made this area of investigation available even to modest university and college laboratories. This is one of the most fruitful and promising approaches to an understanding of reaction kinetics in the fields of both organic and inorganic chemistry, and it has in recent years been the subject of several regional and national conferences, thus reflecting the increasing interest in this topic on the part of chemists of diverse interests.

Isotopic exchange investigations, in general, inquire into the rate and extent of distribution of a given atom in a system that is in chemical equilibrium. By far the most convenient experimental measurement of this distribution exploits the identical isotopic behavior (in most cases) and easy measurability of radioactive nuclides, although enriched stable isotopes with subsequent mass spectrometric analysis have been used in these studies.

In general, to a chemical system at equilibrium, containing one or more distinct ionic or molecular species incorporating a given atom, is added a known amount of reagent in which this same atom has been "spiked" by the substitution of a radiotracer for that atom. The two components—tagged and inactive—are then allowed to remain in contact for a known length of time; one of the components is then physically or chemically separated from the remainder and assayed for radioactivity.

Except for possible isotopic effects arising out of mass differences between the stable and radioactive isotopes, it is assumed that the radiotracer will distribute itself randomly among all of the ions or molecules which carry that particular atom in their structure. The rate of isotopic exchange will thus be the rapidity with which complete randomization of distribution is approached by a tracer in a given system.

In the simplest case, consider a system made up of two components, AB and AC, which do not react chemically (or whose interaction is so slow as to be negligible). If to a known amount of AB is added a known amount of A′C—in which A′ symbolizes the radiotracer—and after a known time A′C is withdrawn from the system and radioassayed, the decrease in specific activity (*e. g.*, counts per second per millimole) of A′C will be a measure of the rate of the isotopic exchange:

$$AB + A'C = A'B + AC \qquad (1)$$

The same result would of course be obtained if the increase in the radioactivity of species A′B had been determined instead.

It has been shown[1, 2] that regardless of the actual kinetic mechanism by which the transfer of A from AB to AC occurs, the rate of appearance of A′ in A′B (or its rate of disappearance from A′C) will follow a first order rate law.

The rate of isotopic exchange for (1) is the rate at which AB becomes A′B, and A′C becomes AC. The amounts of AB and AC undergoing exchange in a given time is of course a function of the relative amounts of AB and AC, as well as the fraction of each which carries the tracer isotope. At isotopic equilibrium, the two exchange rates (forward and backward) are, of course, equal, the *net* rate being zero. The isotopic equilibrium constant is given by the ratio of the total partition functions of the exchanging species, and in the case of diatomic molecules is simply the ratio of the vibrational partition functions of the two reactants carrying the normal and the isotopic atom.

Considering (1), the exchange rate can be expressed as

$$-Rt = \frac{[AB][AC]}{[AB] + [AC]} \ln (1-F) \qquad (2)$$

where the bracketed terms represent concentrations and F is the fraction of exchange defined by

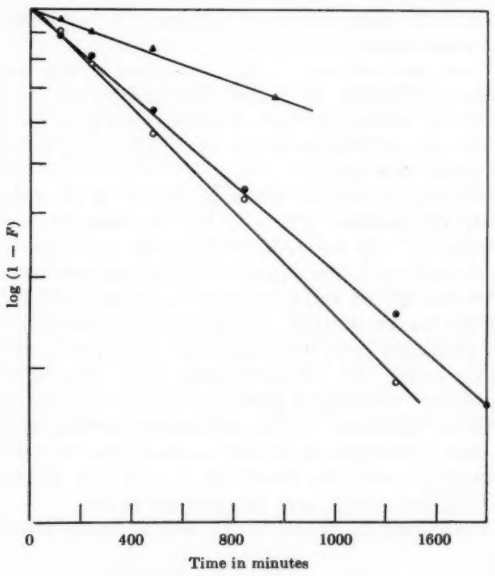
$$F = \frac{S_t - S_0}{S_\infty - S_0} \qquad (3)$$

Here S_t and S_∞ are the specific activities (or isotopic masses for stable isotope experiments) of a selected ionic or molecular species in the exchanging system at time t and at infinite time, respectively. Other expressions for F, to cover special cases, are tabulated in reference 2. In general, S_∞ is calculated on the basis of complete randomization of the radiotracer A′ among all components of the system carrying atom A. S_0 is the "zero-time" exchange, and is a correction for the apparent exchange arising from mixing, the effect of surfaces, the separation method, and other blank

[1] DUFFIELD, R. B., AND M. CALVIN, *J. Am. Chem. Soc.*, **68**, 557 (1946); see also MCKAY, H. A. C., *Nature*, **142**, 997 (1938).
[2] NORRIS, T. H., *J. Phys. & Colloid Chem.*, **54**, 777 (1950).

effects, and may in some cases be very large. For example, in a recent study of the kinetics of the Eu(I)-Eu(III) exchange, the zero time exchange (term S_0 in (3)) was found to be a function of the pH, varying from 7 per cent in 1.6 F hydrogen ion to 20 per cent in 0.1 F H^+. This large effect can be corrected for, however, and it has been pointed out[3] that when the separation-induced exchange and the incomplete separation effects are reproducible, equation (3) can be applied, regardless of the magnitude of S_0.

If ln $(1-F)$ is plotted against time, a straight-line graph should be obtained, and the fit of experimental data to a straight line going through the origin is usually taken as a measure of approach to an ideal isotopic exchange of a given reaction. A typical experimental plot[4] is given in the figure.



SO_2-$SOBr_2$ Exchange

The half-time for the exchange is defined as the length of time necessary for ln $(1-F)$ to reach half of the value at an arbitrary time zero. If this time is incorporated into (2), the isotopic exchange rate is readily calculated[5] from:

$$R = \frac{[AB]\,[AC]}{[AB] + [AC]} \frac{0.693}{t_{1/2}} \qquad (4)$$

Exchange experiments are often designed so that one of the reactants is present in large excess over the other, especially in the elucidation of reaction mechanisms

[3] Prestwood, R. J., and A. C. Wahl, *J. Am. Chem. Soc.*, **71**, 3137 (1949).

[4] Taken from the data of Herber, R. H., and T. H. Norris, Ph.D. thesis, Oregon State College, 1952.

[5] An interesting variation of this equation, correcting for the case of secular equilibrium between two radiotracers, both of which are present in the system, has recently been suggested by R. E. Johnson, *J. Chem. Phys.*, **21**, 1405 (1953).

Activation Energies for Some Isotopic Exchange Reactions

Reaction	*Activation energy, kg.-cal./mole*	*Order of rate step*	*Reference*
NO_2—N_2O_5 (nitrogen)	16.0–19.0	1	11
V(III)—V(IV)	10.7 ± 1.7	2	[a]
SO_2—$SOBr_2$ (sulfur)	13.2 ± 1.0	1	4
Tl(I)—Tl(III)			
(nitrate path)	16.0 ± 0.4	2	3
(H indep.)	17.6 ± 0.4	2	...
(H dependent)	10.3 ± 1.6	1	...
Fe(II)—Fe(III)	9.9	..	[b]
Fe(II)—$Fe(OH)^{++}$	7.4	..	...
Fe(II)—$FeCl^{++}$	8.8	..	...

[a] Furman, S. C., and C. S. Garner, *J. Am. Chem. Soc.*, 74, 2333 (1952).

[b] Silverman, J., and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

by the "flooding technique." In these cases, (4) may be simplified as follows:

$$\text{if AB} >> \text{AC},\ R = \frac{[AC]\ 0.693}{t_{1/2}} \qquad (4')$$

$$\text{if AB} << \text{AC},\ R = \frac{[AB]\ 0.693}{t_{1/2}} \qquad (4'')$$

Half-times, $t_{1/2}$, for isotopic exchanges, may vary from a few seconds to many years. As usual, experimental measurements at both of these extremes require specialized techniques. Concentrations of reagents, temperature, and other rate-determining factors are usually so chosen that the half-time is long compared to the time necessary to ensure mixing of reactants and their subsequent separation preceding the analysis.

Isotopic exchange studies usually concern themselves with the variation in R produced by variations in the concentrations of the components of the system, the pressure, the temperature, and the presence of catalysts for the intermediate reactions reflected by the over-all equation (1).

As in other kinetic studies the effect of variations of pressure and concentration on the rate of exchange will usually allow the formulation of an exchange reaction mechanism, the order of the reaction with respect to a given reactant being determined by the "flooding technique."

The measurement of the variation of R with the absolute temperature, T, allows a calculation of the activation energy by use of the well known Arrhenius equation, which can be written as

$$E^{\pm} = 2.303 \times 1.986 \times \frac{d(\log R)}{d(T)} \qquad (5)$$

which gives $E^{\pm}$ in terms of kg.-cal./mole.

Activation energies for isotopic exchange reactions are not well known, but appear to be on the order of 10–20 kg.-cal./mole for reactions with measurable half-times.

Some recently reported activation energies are listed in the table.

It has recently been pointed out in an interpretation of the significance of isotopic exchange in rate theory[6] that the rate of distribution of an atom for its (lighter or heavier) stable isotope can be evaluated if the partition functions for the normal and activated states are known. Partition functions for isotopic exchange reactions have recently been discussed in some detail [7, 8, 9, 10] and various terms for the calculation of the entropy, enthalpy, and heat capacity collected in tabular form.

[6] EYRING, H., AND F. W. CAGLE, *J. Phys. Chem.*, **56**, 889 (1952).
[7] BIGELEISEN, J., *J. Chem. Phys.*, **21**, 1333 (1953).
[8] BIGELEISEN, J., *ibid.*, **15**, 261 (1947).
[9] BIGELEISEN, J., *ibid.*, **17**, 675 (1949).
[10] BIGELEISEN, J., *J. Phys. Chem.*, **56**, 823 (1952).

Recent applications of isotopic exchange have included studies in the kinetics of the NO_2—N_2O_5 nitrogen exchange,[11] a number of investigations of the rapidity of exchange involving electron transfer,[12] exchange studies in acetic acid and acetic anhydride,[13] liquid sulfur dioxide[14] and liquid hydrogen sulfide, and geologic age determinations from sulfur isotope ratios.[15]

[11] AMELL, A. R., AND F. DANIELS, *J. Am. Chem. Soc.*, **74**, 6209 (1952).
[12] LIBBY, W. F., *J. Phys. Chem.*, **56**, 863 (1952).
[13] EVANS, E. A., J. L. HOUSTON, AND T. H. NORRIS, *J. Am. Chem. Soc.*, **74**, 4985 (1952).
[14] NORRIS, T. H., R. E. JOHNSON, AND J. L. HUSTON, *ibid.*, **73**, 3052 (1951). See also Ref. 4.
[15] TUDGE, A. P., AND H. G. THODE, *Can. J. Research*, **B28**, 567 (1950).

EVALUATION OF AN UNDERGRADUATE CHEMISTRY CURRICULUM

WILLIAM F. HART
Lafayette College, Easton, Pennsylvania

DURING the spring semester of 1953 Lafayette College undertook an intensive self-study program to determine the optimum curricula for preparation for careers in the various professions. This study was made possible by a grant from the Fund for the Advancement of Education (Ford Foundation). Eight commissions were established to study various areas of preprofessional interest, each being composed of faculty members representing the departments concerned, alumni distinguished in the respective fields, and impartial expert consultants not connected with the College.[1]

The Commission on Careers in Science defined its problem as follows: to determine the optimum balance between the general and specialized courses which will best prepare Lafayette graduates for careers in science. Further, the Commission was charged by the terms of the study to consider the curricula taken by students in recent years, the success of these students in graduate school, and, as far as possible, their success in their chosen careers. The Commission ruled out as beyond the scope of the problem such very important considerations as admission policies, quality of faculty, and facilities for instruction, realizing that each of these areas would be a fertile field for a major study. The Commission was also instructed to devote particular attention to the B.S. in chemistry and B.S. in physics curricula. This paper will be limited to a summary of the Commission's report dealing with the B.S. in chemistry curriculum.

Seven procedures were agreed upon to implement the solution of the problem. First, a census was made of all graduates who had received the Ph.D. degree in chemistry or who were candidates for this degree, and the members of this group were requested to evaluate their undergraduate training. Twenty-seven men, in addition to alumni on the faculty and Commission, were contacted and from this number 20 responses were obtained.

The replies received from this group were a valuable contribution, as they were personal and sincere and showed much mature thought. Only one man considered his training inadequate for graduate work and inferior to the training of his colleagues of the same age group. All of the others rated their training as adequate or more than adequate, and equal or superior to that of their colleagues. Suggestions accented by repetition included language training in both French and German, an increase in instrumentation in quantitative analysis, the addition of a course in advanced

[1] Personnel of the Commission on Careers in Science included: outside consultants, James P. Brusie, Charles L. Fleming, Jr., Ralph K. Gottshall, John W. Landis, Basil McCabe, Joseph B. Quig, and John W. Reynard; faculty members, Mark Bålderston, Winfield Keck, and William F. Hart.

inorganic chemistry, the addition of a second course in physics, and the inclusion of more physical organic in advanced organic chemistry. Several men suggested that the A.B. curriculum with a major in chemistry is better preparation for graduate school than the B.S. in chemistry course.

The second procedure was to inquire of the graduate departments of chemistry in selected universities concerning newer requirements and suggested curricula to best prepare for graduate study. The heads of representative graduate departments of chemistry, in which departments several Lafayette alumni have pursued their graduate work, were questioned and asked to state their opinions.[2]

There was a considerable degree of unanimity in the expressions of this group of authorities. Their recommendations included a course in communications (oral and written reports), a minimum of mathematics through calculus (physical chemists require differential equations and advanced calculus), advanced organic chemistry, including one term of synthesis and one term of reaction mechanisms and physical organic, a second year of physics, reading knowledge of French and German, and good courses in thermodynamics, mechanics, heat, and electricity for physical chemists. One department head stated that the minimum requirements for accreditation by the A. C. S. are sufficient preparation.

Third, a survey was conducted of the requirements for admission to graduate school by a study of catalogues of 11 representative universities. In a few cases this was supplemented by personal interviews with a responsible officer of the graduate school.

A study of catalogues was not particularly helpful, as requirements stated are always minimal, and each school allows itself considerable leeway in selecting the desired number of students from available applicants. It was determined that the better graduate schools require a distinctive record, *i. e.*, at least an 85 cumulative average, and that previous experience with graduates of a college is taken into consideration. It is important to direct only the best men to distinguished institutions as one poor record will ruin chances of applicants for many years later.

The graduate record examination as a requirement is relatively new, but is being given increasing consideration. A few institutions now require it and others strongly urge it. It is probable that in a few years it will be required by most graduate schools.

Two factors are by far the most important in securing admission to graduate school. These are the undergraduate cumulative average and the letters of recommendation. Graduate departments are not as much concerned with the particular courses completed as with a man's record of achievement.

A man with a brilliant record will be readily admitted even if he has several course deficiencies. This may require an additional year's work, but the department will admit him on this basis. Letters of recommendation are given great consideration.

The recent Wesleyan Report[3] and similar surveys reveal that most men who obtained Ph.D.'s in science came from small and sometimes obscure institutions. Further, the professional record of these men after several years is better than that of men from larger institutions. For this reason the best graduate schools do not hesitate to admit men from smaller institutions, if they have an outstanding record and/or are highly recommended.

Fourth, attention was devoted to the requirements for accreditation of graduates by the American Chemical Society.[4]

It was noted that the Lafayette Chemistry Department is accredited by the American Chemical Society, and that the B.S. in chemistry curriculum exceeds the minimum requirements for certification of graduates by the Department to the Society as eligible for junior membership.

The Commission felt that the A. C. S. requirements are minimal, and do not preclude the desirability of additional professional courses. However, it is interesting to note that in this survey one head of a graduate department of chemistry and the personnel directors of two chemical corporations stated that the minimum A. C. S. requirements are sufficient undergraduate preparation.

Fifth, an evaluation of undergraduate training was sought of alumni who entered industry upon graduation. A total of 476 questionnaires were sent to alumni whose occupations were known to be in the field of industrial science. From these were received 100 replies, and 35 of these were from graduates in chemistry. Nearly all of this group expressed satisfaction with their training, the great majority rating their professional preparation as excellent or good, and superior or equal to colleagues of their own age group.

Suggestions on which there was considerable unanimity included: more instrumentation in advanced quantitative analysis, qualitative organic analysis (given in recent years), quantitative organic analysis, a course in communications (to include training in written and oral reports), a course in personnel relations (human relations and labor relations), and applied statistics for design and control of research.

Other suggestions offered by several men included: more electronic mechanisms in advanced organic chemistry, courses in advanced inorganic chemistry, biochemistry and public speaking, and an organized and systematic counseling and guidance program.

[2] Replies were received from the heads of the graduate departments of chemistry of Cornell University, Harvard University, University of Illinois, Massachusetts Institute of Technology, The Pennsylvania State University, and Yale University.

[3] KNAPP AND GOODRICH, "Origins of American Scientists," Chicago University Press, 1952.

[4] "Minimum Standards Used as Criteria in Evaluating Undergraduate Professional Training in Chemistry," American Chemical Society, Committee on Professional Training, 1949.

Sixth, the opinions of industrial personnel officers were sought. A personal letter was addressed to the directors of technical personnel procurement of 53 nationally known companies, research institutes, and government agencies that employ scientists. These men were asked to comment upon specific backgrounds of training lacking in recent graduates and to state whether these deficiencies could be corrected by curricular adjustment.

They were also asked to list specific courses for addition or elimination, to state whether or not they favored an increase in liberal-arts courses at the expense of reduction in science courses, and to recommend the amount of mathematics they felt necessary for a successful career in chemistry. Copies of the B.S. in chemistry curriculum were enclosed and these officials were asked to direct their recommendations to the curriculum, and were invited to offer anything they cared to on related points.

From this group 33 replies were received, which constituted a highly satisfactory return, but what was more important, the quality of these replies made them outstanding and of great value to the study. In many cases the inquiry was referred to research departments, and the director of research in consultation with selected associates considered the problem, and made many valuable suggestions and criticisms. In a number of cases model curricula were proposed in considerable detail.

The returns from this group, which represent the considered opinion of a large number of highly qualified individuals, were much more critical of the attitudes of recent graduates than of their formalized training. The present generation of college graduates who have lived all of their lives in an economy committed to a "from-cradle-to-grave" philosophy were condemned in no uncertain fashion for their lack of willingness to work or to accept responsibility, for their disregard of punctuality and even for their suspicion of the profit motive of our capitalistic system. It was said that as a group they are more concerned about automatic salary increases and social security benefits than they are in giving an honest day's work for an honest day's pay. It was admitted that curriculum changes cannot cure evils such as these, but the faculties were charged to attempt to correct them by forcing undergraduates to work harder, by their own example as well as by precept.

Practically unanimous criticisms which more properly belong on the doorstep of the colleges were the charges that recent graduates can "neither read nor write" and that they cannot think in logical fashion, much less present ideas in writing or orally. The unanimity of these criticisms destroys any doubt as to their reality, and the commission devoted much thought in an effort to find corrective curricular changes. It was conceded by most sources that these difficulties stem back to grade and high schools, but that the colleges must do more to alleviate the condition than merely to attempt to put more pressure on the secondary schools. This would seem to be the number one academic problem facing the colleges today. To summarize the proposals of this group directed toward the curriculum: there was an almost unanimous recommendation of a course in communications (written and oral reports and business letters) and strong support for courses in public speaking and elementary economics from a practical business standpoint, with a lesser number of suggestions to include accounting and marketing. There was strong support for increase in the liberal-arts content of the curriculum, suggested additions including history, psychology, English composition, English literature, philosophy, and political science.

On the other hand, there was decided disagreement as to whether the mathematics content should be lightened or kept intact, as to whether modern languages should be required or dropped, and as to whether metallurgy should be retained or dropped. Many industrialists now feel that a reading knowledge of foreign languages is a specialty and that a large company can retain a specialist to make needed translations. There was support for a second course in physics but disagreement as to whether technical courses should be reduced, in spite of the desire to increase the liberal-arts content. One company felt strongly that entrance requirements should be stiffened so as to make elementary chemistry unnecessary, and that hour requirements should be increased to 24 hours' classwork per week, counting one hour of laboratory as one-half hour of classwork.

The seventh and final procedure was to compare the B.S. in chemistry curriculum with those of other high ranking colleges and universities. Considerable time was spent in the study of catalogues of institutions of all types. This kind of study cannot be readily analyzed or tabulated. For that reason, it was decided to compare and tabulate on a percentage basis the relative proportions of technical courses and humanities or social sciences offered in the curricula of representative institutions offering the degree of B.S. in chemistry. It is to be noted that the B.S. degree is more commonly given in institutes of technology than in colleges of arts and science. Different systems of calculating credits and semester hours complicated the tabulations, but it is believed that the percentages arrived at give a fair picture of the situation, although in some institutions certain electives may be taken in either technical or liberal-arts subjects. Military science and physical education were omitted in all cases to reduce confusion in arriving at total course credits. Mathematics was included in technical courses; English composition and modern languages were included as humanities.

On this basis the four-year curriculum at Lafayette contained 25 per cent humanities or social sciences. Percentages of liberal-arts courses in comparable curricula were: Massachusetts Institute of Technology, 23.8 per cent; University of Wisconsin (general op-

tion), 28.7 per cent; Carnegie Institute of Technology, 22.6 per cent; Case Institute of Technology, 22.6 per cent; and Brown University, containing features which make it somewhat different from the other institutions under comparison, 37.5 per cent.

From the above comparisons it may be seen that Lafayette's B.S. in chemistry curriculum was not out of line with respect to the proportion of liberal-arts courses to technical courses, but that the liberal-arts content was slightly lower than that of other comparable institutions and could well be increased somewhat.

The Commission, drawing on the knowledge of its members, made a number of recommendations to the Lafayette administration; these were based on a careful review of those secured through the procedures described above. These included a group of specific recommendations dealing with curricular changes and a second group of general recommendations. The recommendations involving curricular changes were as follows:

(1) To reduce the modern language requirement from three years to two, providing room for one year of a second language or a second course in physics.

(2) To reduce qualitative analysis from a full year to one semester, providing space for a one-semester course in advanced inorganic chemistry, to be given in the junior year.

(3) To reduce organic chemistry from a total of five semesters to four, the advanced organic chemistry to be reduced to one semester of theoretical organic and this to be followed by one semester of qualitative organic analysis, already in the curriculum.

(4) To combine physical chemistry laboratory, previously given as a separate course, with physical chemistry.

(5) To consider the formation, with the Physics Department, of an interdepartmental course in instrumentation, to be an alternative to advanced quantitative analysis.

(6) To change chemical literature into a two-hour seminar course, to include training in written and oral reports as well as in the use of the library.

(7) To create the possibility of scheduling four and one-half full-year elective courses in the humanities and social sciences in the junior and senior years, as compared with two year-courses previously available.

(8) To make available as elective courses advanced organic preparations, honors, and courses in chemical engineering.

Considering the severe and almost universal criticisms of the attitudes of recent graduates with regard to their lack of willingness to work or to accept responsibility, and of their inability "to read or write" or think in logical fashion, the Commission felt that changes in the curriculum alone could not effect the desired improvement. Hence the following general recommendations were also made to the Lafayette administration.

(1) Each department should require in the content of all courses, so far as possible, the presentation of written and oral reports. Such reports should be graded on general form, use of proper English, punctuation and spelling, and fluency and lucidity of expression, as well as on subject matter content.

(2) Each department should designate one professor who has demonstrated a sincere interest in counseling to give preprofessional guidance to the students within that department. This professor's teaching duties should be reduced proportionately for this work. Guidance work should be intensified at the time of selection of the major field in the case of A.B. students.

(3) More space in the catalogue should be devoted to describing the curricula and electives which will give the best preparation for graduate school or for direct entry into industry.

(4) The carrying on of research by members of the faculty should be encouraged. This will not only improve the quality of teaching but will arouse the intellectual curiosity and interest of the students.

(5) The liaison between the College and industry should be strengthened by: (*a*) arranging plant trips in connection with course work; (*b*) arranging summer employment for students in industry, particularly following the junior year (the departmental guidance expert might assist in these arrangements); and (*c*) arranging summer employment for professors in industry to refresh their knowledge of current industrial practices.

In October, 1953, a revised B.S. in chemistry curriculum was drawn up by the Chemistry Department, and was approved by the Arts and Science Curriculum Committee and by the Faculty. This revised curriculum effectively implemented all of the specific curricular recommendations of the Commission, with the exception of the formation of an interdepartmental course in instrumentation, which proposal is under consideration. A number of the other Self-study Commissions also made general recommendations. They were similar to those proposed by the Commission on Careers in Science, and these are under study by the various faculty committees and the desired improvements will undoubtedly be arranged.

It is realized that the Lafayette B.S. in chemistry curriculum, either before or after this revision, has no unusual features, and does not differ markedly from that of many other high-ranking colleges and universities.

THE EXCITEMENT OF EXPERIMENT[1]

ROBERT K. SUMMERBELL
Northwestern University, Evanston, Illinois

THE originators of chemistry delved into that unknown field only because they found experimentation exciting. Like the ham radio operators and amateur photographers of today, they devoted time and energy to experimentation because it was fun. The graduate students and young university staff members today work impossibly long hours and make unbelievable personal sacrifices for the same reason. Experiment, when it is truly experiment, when the individual asks a question of nature and finds the answer from nature, is as exciting as it ever was. It is the most powerful tool for motivation in the hands of our science instructors, but the laboratory work and the demonstrations as used by many of us actually turn students away from chemistry. The most important responsibility of today's chemistry teachers is to give the students the same sense of excitement that motivated the pioneers of yesterday and still motivates the researchers of today. The laboratory work presented by most of us fails dismally in this objective. The current shortage of chemists is in no small measure a result of the inane and stultifying laboratory work to which we subject our students.

WEAKNESS OF STANDARD EXPERIMENTS

We chemistry teachers often deceive ourselves as to just how worth while many of our standard laboratory experiments are. Because of the orderliness of nature, our optimism is seldom subjected to a critical test. Early in my own teaching career I was fortunate enough to have such a test forced upon me, and the results were so illuminating that they are worth reporting here. The course in which I was conducting a laboratory was the typical "Smith" course of a generation ago, and the experiment in question was one of the better ones for bringing out broad generalizations. The students had already learned by observation and study of the text that zinc was capable of reducing nitric acid to ammonia, the lowest oxidation state of nitrogen. In this particular experiment the student was instructed to add a few drops of concentrated sulfuric acid to powdered zinc and observe the gas evolved. The text made quite a point of the fact that H_2S, which contains sulfur in its lowest oxidation state, would be given off, and emphasized the analogy to nitric acid going to ammonia. On this particular occasion, forty students "observed" the predicted H_2S and reported it in their notebooks, but one rather poor student was absent and made up the work at a later time. Since he had either not read or not understood the text, he had no preconceived ideas and reported that hydrogen was evolved. While checking notebooks, I came across this statement, called the student in and explained to him that by scientific standards his crime of recording as observations things that he could not possibly have seen was extremely serious. He, however, insisted that the evolved gas popped like hydrogen and had no odor of H_2S. I referred the matter to a senior professor who had the good sense to challenge the student to reproduce his results. This he proceeded to do, much to the astonishment and chagrin of the senior professor and myself.

Investigation revealed that the zinc being used that year was the then new electrolytic kind, and that impurities present in the ordinary zinc previously used had catalyzed the reaction that produced H_2S. The new electrolytic zinc gave only hydrogen. This new zinc which gave only hydrogen had been used by the forty bright students who "observed" the hydrogen sulfide that simply was not there.

I had a similar experience recently. A "known" practice solution in qualitative analysis was advertised to the students as containing ferrous ions. A lazy assistant had put on the side shelf an old solution prepared the previous year in which the ferrous ions originally present had long since been oxidized to ferric. Before we discovered our mistake, a goodly number of bright students "found" the ferrous ions that were not there.

We chemistry teachers sometimes defend our routine laboratory work by saying that the student is being taught by "observation." Any experienced chemistry teacher can cite numerous examples parallel to those described. No student ever learned to make observations by doing routine experiments that simply confirm statements of the text or of the instructor.

THE UNEXPECTED TWIST

There is little excitement in simply confirming a minor statement in a text. On the other hand, there may be considerable interest in unexpectedly elucidating a more diffuse concept. In our elementary course we have a standard experiment which verifies the gas law $P/T_{abs} = K$. The student measures the pressure of a sample of gas at various temperatures and tests this relationship. Canceling errors contribute to a phenomenally good result. The student gains a desirable sense of accomplishment and learns something about the nature of a constant. On one

[1] From a lecture delivered on July 15, 1953, at the Institute for the Teaching of Chemistry, St. Louis University, St. Louis, Missouri.

occasion I happened to suggest to a superior student who had finished the work ahead of time that by graphing his centigrade temperatures against his observed pressures he could arrive at his own value of absolute zero. He did so, and by lucky chance, arrived at a value very close to the accepted one. He communicated his enthusiasm to several neighbors who treated their data similarly with generally good results. The conflagration spread through the laboratory, and a session that had been rather stolid was converted to a worth-while experience for the students and an inspiring one for the instructor. I have experimented with this idea several times since, and although the results have been satisfactory, they have never been quite as exhilarating as they were on that first accidental venture. It contained an element of personal participation on the part of both student and instructor that could never be recaptured. It is my firm conviction, however, that this type of unexpected twist could be given to many of our standardized experiments if the instructors were sufficiently intelligent and alert.

USE OF UNKNOWNS

Almost every teacher of our now standard college freshman chemistry courses will testify that the course comes to life when qualitative analysis is reached. This phenomenon is not a result of the rather complex theory that most of us introduce nor to the possible utility. Rather it results from the fact that we are introducing the student, often for the first time, to the excitement of experiment. He has a real, if somewhat artificial problem, the contained ions of his unknown solution. He proceeds to ask questions of nature by doing experiments, and nature answers. The teaching must be very inferior or the student very stupid to escape some of the excitement of experiment.

When qualitative analysis was first introduced into the curriculum, I doubt very much that the excitement of experiment was the dominant factor in the minds of the originators. At that time it was the only method of analysis available, and competence as an analyst was important to the practicing chemist. Spectroscopy, polarography, and specific organic reagents have almost completely replaced it in industry. Even as a teaching device, qualitative analysis is far from ideal. The techniques are too repetitive to constitute good teaching practice. Not enough thought is required, since a mediocre student, by slavishly following directions in a cookbook fashion, will emerge with satisfactory results. In spite of the unknowns, interest lags perceptibly toward the end of the course.

We have an experiment under way at my institution that we hope will overcome some of these objections. Toward the end of the term each student will be given a sample of a cation not traditionally included and for which no provision is made in the scheme. He will be asked to study the chemistry of this element, evolve methods of testing for it, determine its presence or absence in a couple of unknowns, and submit a comprehensive written report concerning his findings. If results are encouraging, we shall report on them at a later date.

The element of the unknown, so valuable as a teaching tool, can be introduced into other more significant experiments. As chemistry teachers, we should be devoting time, energy, and creative ability to doing so. Determination of molecular weight by vapor density is a standard college experiment. The student determines the weight, volume, temperature, and pressure of a sample of matter in the gaseous state by direct or indirect measurements, and from these results calculates the molecular weight. In the older procedures all of the students used the same standard substance such as chloroform or carbon tetrachloride. The students were graded on results, so that there was a definite premium on dishonesty. The procedure contained inherent errors, so that only by modifying data could the student be sure of receiving the maximum grade. Since the answer was known, there was a strong temptation to fake results. Only occasionally when an inferior student made an arithmetical mistake was such dishonesty detected. We have found that by introducing unknowns the value of this experiment is greatly increased. There is no longer any problem of honesty. The student is asking a question of nature, and the *only* way he can arrive at an answer is to make observations. He does so, and a good result gives him a real thrill. He has experienced the excitement of experiment.

The device of introducing unknowns into standard experiments is a simple and attractive concept in theory, but it is far from simple in practice. A great deal of hard work is involved in selecting appropriate unknowns in adequate variety, testing them under student laboratory conditions, and dispensing them in such a fashion as to reduce bookkeeping errors to the minimum. To be effective as a teaching device the unknown must be really unknown to the student and known with absolute certainty by the instructor. These details require time, imagination, and creative energy, all commodities that unfortunately are in limited supply under practical teaching conditions.

Some of us spend considerable time in grading laboratory reports which may or may not represent the personal observations of the students who have submitted them. Often they are copied from a laboratory neighbor, or from the notebook of a student who took the course the preceding year. Some laboratory manuals follow the text so closely that practically all of the questions can be answered after a superficial reading of the corresponding section of the text. Some of the time needed for instituting a program of unknowns can be garnered by eliminating such useless checking of laboratory reports.

Any claim of originality or newness for all these ideas would be preposterous. Numerous colleagues and acquaintances have been experimenting along

these lines as long as the author can remember, and the newer college laboratory manuals, especially those written by younger men, make increasing use of unknowns. One that has come to my desk since work on this paper was started demands that an unknown be solved every time that a student comes to the laboratory. It is my contention that the idea could and should be explored at more elementary levels.

OTHER DEVICES

There are other effective means of making experiment exciting to the students. Any student worth bothering with enjoys using superior equipment. He enjoys it even more if he understands what he is doing. Even as simple a thing as a fine balance will serve this purpose, but for the equipment to remain superior calls for constant vigilance on the part of the instructor. Rigid rules of cleanliness and manipulation must be enforced. When several instructors use the same laboratory, responsibility for the condition of a piece of special apparatus must be assumed by one individual. The apparatus must be in first-class condition every time a new student starts to use it. Students, with few exceptions, will cooperate in maintaining good apparatus if the instructor does his share.

Our college experience with the course in quantitative analysis bears on this point. When I was a student in such a course 25 years ago, the laboratory work consisted of an endless procession of precipitations, weighings, and titrations. In the modern course, such techniques are limited to the introductory portion, and during the year the students use pH meters, colorimeters, high-temperature combustion furnaces, and gas analysis and electrodeposition equipment. I have no evidence as to whether or not all this produces as competent analysts as the old regime, but I am sure that more of our graduates are looking with favor on analytical chemistry as a possible vocational field.

Inadequate financial resources will limit, but not obliterate, the value of this suggestion. In addition to his other extracurricular duties, the teacher must become a salesman and convince either his administration or friends of the institution that such expenditures are wise and profitable. New balances for the chemistry laboratory could be as important as new uniforms for the band.

The glamorous aspects of chemistry, while touched upon in class sessions, have received too little attention in the laboratory. Of course, it is a bit beyond present possibilities to construct an atomic pile, but several practical experiments involving radioactivity have been developed. If a Geiger counter and several samples of radioactive ore are available, it is perfectly feasible to set up an experiment in which the relative activity of the different ore samples may roughly be evaluated. Even a rather inactive sample of carnotite will take its own picture if placed in contact with a wrapped photographic plate, so that in the absence of a Geiger counter the much cheaper photographic technique may be used. One of my colleagues often takes some dental X-ray film on his fishing trips and tests the rock formations of the surrounding countryside. He has yet to find a uranium deposit, but he enjoys himself thoroughly, even on those rare occasions when he doesn't catch any fish.

Several of the simpler dyes, such as phenolphthalein, are readily prepared in the laboratory. If a variety of homologues of phthalic anhydride and of phenol are made available, a minor group research project could be developed. Since the colors of the various derivatives will not be listed in any book available to the elementary student, the element of asking a question of nature and determining the answer by observation would be present. Adequate experiments in the fields of plastics, synthetic drugs, and synthetic fibers are not beyond the realm of possibility.

The less glamorous and more practical aspects will appeal to some students. Almost every elementary course includes an acid-base titration. Why not have the students evaluate various brands of vinegar or of household ammonia available at the local grocery?

There is a serious road block to all such suggestions: they are not efficient. If "the ground is to be covered," how can we afford to devote a couple of laboratory periods to the titration of household ammonia? The answer is, of course, that the ground will not be covered. Students who have been subjected to such a hodgepodge of miscellaneous projects will perhaps not score quite so well on standardized tests, on college board examinations, or in the examination portion of the invaluable Westinghouse competition. Perhaps, however, more of them will have an appreciation of the real nature of science. If the truly exciting nature of experiment can be brought home to the students, we can stop worrying about the shortage of chemists.

THE PERSONAL TOUCH

For several years I have experienced little difficulty in teaching the calculation and significance of molecular formulas. Each year when we come to that portion of the course I take to the lecture a sample of one of the new compounds that one of my graduate students has prepared. I explain how the compound is analyzed, calculate the simplest formula from the actual analytical data submitted by our microanalyst, and point out the necessity for determining the molecular weight. A couple of weeks later, when the class is studying molecular weights, I discuss the various possible applicable methods for this particular new compound, and my reasons for choosing one rather than the other. The molecular weight and molecular formula are then calculated directly from research data copied on the board from a student research notebook. The method never fails to excite interest. For months students will ask all sorts of questions as to the progress of our research. One of the great advantages of this method of presentation is that it dramatizes the idea that chemistry has much unfinished business. Few textbooks succeed in conveying this idea.

This particular mode of teaching this specific type of problem may not be available to many secondary-school teachers, since only a few of us will have in our possession the requisite new compounds in which we have a personal interest. But chemistry touches so many phases of the lives of all of us that the alert teacher will think of numerous ways of introducing his personal hobbies and interests into the course in such a way as to vitalize subject matter that is otherwise dry and boring.

Most essential, the instructor must serve to himself a liberal portion of excitement by continually experimenting with new techniques of teaching. Excitement is the most contagious and the least curable of diseases. Those affected with this disease are never cured and few are immune. (Those unfortunate individuals who are congenitally immune should be selling insurance or washing bottles, not teaching.) If we allow ourselves to become bored with our jobs of teaching, our students will most certainly be bored with the subject matter that we present. The excitement of experiment is as essential to the professor as to the student. Perhaps in the science fields educational administrators should give considerable weight to evidence that the teacher is experimenting with modification of old experiments and the introduction of new ones.

UNSOLVED PROBLEM

The evaluation of the effectiveness of teaching methods is one of the most difficult of educational problems, particularly when we are trying to measure such intangible things as student motivation. As scientists we demand measurements that can be expressed numerically. Because of the pioneering work of such a group as the Examinations Committee of the Division of Chemical Education, we know pretty well how to test efficiently such things as subject-matter retention, ability to balance equations, or facility in working mathematical problems. Tests are even available for measuring competence in laboratory manipulations, or ability to apply scientific reasoning processes to a specific situation. All of these things are important and the proved validity of such tests is encouraging, but no satisfactory method of measuring motivation has come to my attention. Data can be collected as to the proportion of students electing advanced work in the field, but such data are subject to much random variation and are hopelessly out of date by the time significant amounts have accumulated. There are, however, a number of less precise, but perhaps more significant indications that are available. Do the students ask questions during, and, more important, after the class? Are the students difficult to eject from the laboratory? Do they use library references and ask for more? Do they inquire about the possibility of a career in science? Do they attend unrequired public lectures in the field? Some of these criteria may be better than formalized tests as to the adequacy of the teaching. A fair portion of students who have been taught effectively should do all of these things.

From antiquity comes the classic, although perhaps apocryphal, story concerning my theme. King Hiero, having furnished his artisans with gold for a new crown, became suspicious that they were substituting cheaper metals. He assigned the problem to Archimedes, but the textbooks of the era held no solution. Archimedes happened to notice the buoyancy of his own body while bathing, and from this not very uncommon experiment evolved the principle that every schoolboy associates with his name and the solution of Hiero's problem. Without bothering about such mundane matters as garments, he rushed about the streets shouting, "Eureka!" It is optimistic to expect our elementary students to leave the laboratories in this extreme state of agitation, but I have seen research students in the halls of university laboratories in a similar psychological, if not physical, condition. The superior teacher can and should introduce some of this same excitement of experiment into elementary laboratory courses.

A SIMPLE, AUTOMATIC GAS BURET

ROBERT D. GOODWIN
Air Reduction Company, Inc., Research Laboratories, Murray Hill, New Jersey

THE measurement of rate of evolution of a gas is a procedure of very general applicability. For low rates it is convenient to employ a buret. This requires continuous manual or automatic adjustment to preserve a constant pressure in the system under study. It is accepted practice to employ manostatic devices involving electric relays for control of the amount of confining liquid in the buret.[1]

Upon inquiring whether such paraphernalia are necessary, it was found that automatic control could be obtained simply by suspending a leveling bulb from a spring.[2]

It is the aim of this communication, therefore, to illustrate for pedagogical purposes that the most simple equipment may be surprisingly versatile, and that in the design of experiments elementary laws of hydrostatics find repeated application.

The physical system requiring analysis is illustrated by the figure, in which A represents a gas buret and B represents a leveling bulb suspended from a spring. It is the purpose of the analysis to find the relationship between the parameters of the system imposed by the condition that the pressure in the buret shall be independent of volume. Symbols employed have the following meaning:

a, cross-sectional area of cylindrical gas buret, cm.^{2}
D, density of confining liquid, g. cm.$^{-3}$
h, height of liquid in leveling bulb, cm.
H, height of liquid in buret, cm.
j, mass per unit length of flexible connecting tube, g. cm.$^{-1}$
k, spring constant, g. cm.$^{-1}$
L, buret length, cm.
p, gas pressure in leveling bulb, g. cm.$^{-2}$
P, gas pressure in buret, g. cm.$^{-2}$
Q, $k + j/2$, g. cm.$^{-1}$
r, ratio of area of cylindrical leveling bulb to buret area.
v, gas volume of buret, cm.^{3}
x, downward displacement of leveling bulb, cm.

For simplicity, assume $H = L$ and $h = 0$ when $x = 0$.

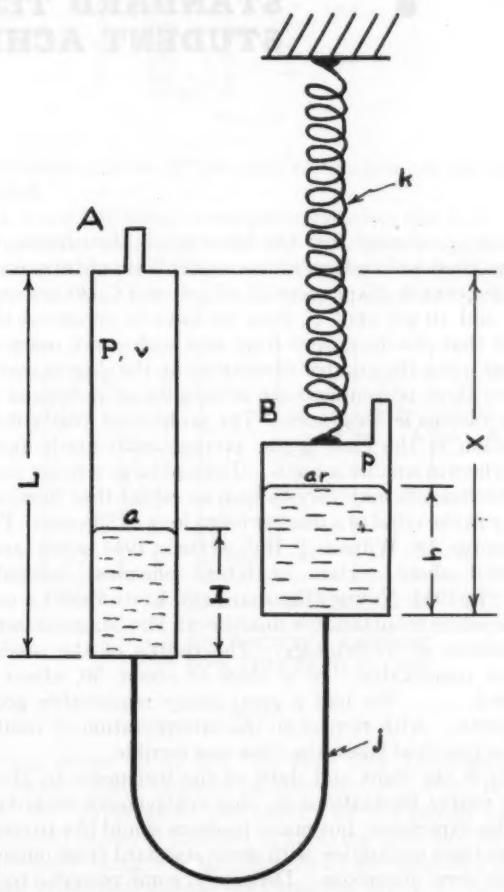
The significant apparatus parameters are a, r, Q, and D. Three variables of displacement, namely, x, h, and H must be eliminated. Only three relations obtain among the variables; their elimination is possible by a single differentiation, representing the required condition, since the equations are of the first degree. The three relationships are the following: (1) total volume of liquid is constant; (2) difference of liquid levels is determined by gas pressures; (3) forces on the leveling bulb at rest are in balance.

$$a(H + rh) = \text{const.} \quad (1)$$
$$P - p = (L - H + h - x)D \quad (2)$$
$$arhD = kx + jx/2 \quad (3)$$

It is assumed that gas pressure, p, in the leveling bulb is constant. The variables then are eliminated by the condition $dP/dv = 0$, noting that $dv = -adH$. The result is

$$aD/Q = 1 + 1/r \quad (4)$$

We see that a leveling bulb of large cross section is desirable in that a minimum spring extension equal to the buret length will be obtained thereby. When an approximately correct spring constant, k, has been ob-



Automatic Gas Buret

[1] HODGINS, J. W., AND R. B. HARVEY, *Can. J. Research*, 24B, 81–2 (1946).
[2] WILSON, L. D., *Ind. Eng. Chem., Anal. Ed.*, 8, 488 (1936).

tained in practice, final adjustment of the system may be achieved by means of small variations in the diameters of the flexible tube and of the leveling bulb. Any small rod inserted in the leveling bulb will decrease the liquid surface area. For mercury in a 20-mm. diameter buret, the spring constant required will be about 40 g. cm.$^{-1}$

It would be instructive for students to discuss the condition for which $P = p$, namely, that the buret pressure equal the external pressure upon the leveling bulb. The reason why the mass of the empty bulb does not appear in these expressions involves an *understanding* of the behavior of an ideal spring. What information is necessary to determine the length of spring required? The question whether this system is in stable equilibrium; the dependence of sensitivity upon density of confining liquid; and the time of response to changes in the rate of gas evolution—these questions should afford material for stimulating interest in the practical applicability of this useful device.

STANDARD TESTS FOR THE EVALUATION OF STUDENT ACHIEVEMENT

GEORGE E. F. BREWER
Marygrove College, Detroit, Michigan

If it is assumed that the letter-grade distribution in large classes of undergraduate students should approach 10 per cent A, 20 per cent B, 40 per cent C, 20 per cent D, and 10 per cent F, then we have to recognize the fact that the deviations from any such curve must be large when the number of students in the class is small, since these percentages are arbitrarily proportioned to the various letter grades. The problem of yearly fluctuation in the class grade average particularly faces teachers in smaller schools. Even in large schools class achievements may vary to such an extent that they can stay in the mind of a teacher for as long as 30 years. For example, Dr. William T. Hall wrote in 1944, when questioned about certain analytical chemical methods: ". . .In 1914, Noyes, Blanchard and I introduced a new procedure in qualitative analysis at The Massachusetts Institute of Technology. The results of the session were remarkable. In a class of about 50, about 5 failed. . . . We had a great many remarkably good reports. . .with respect to the interpretation of results on a practical basis, the class was terrible. . . ."

It is the right and duty of the instructor to allow for yearly fluctuations in class achievement according to his experience, but many teachers would like to compare their evaluation with some standard from outside their own classroom. Definitely, some powerful tools for the evaluation of class achievement are the A. C. S. cooperative tests.[1] Committees of well known teachers of chemistry develop these multiple-choice machine-scoreable tests every one or two years in many fields of instruction.

These cooperative tests—when they are of the five-choice single-answer type—are scored by the "right minus one-fourth wrong" ($R-W/4$) formula, to prevent the influence of wild guessing, which, by the law of averages, would yield one right answer at every fifth attempt. The Examinations Committee requests all instructors to report the grades of all the students: these are then pooled and evaluated statistically. Percentile norms are then published setting the average $R-W/4$ score at 50 per cent, allowing the evaluation of an individual student in terms not only of his own score but in comparison to students from a group of schools.

Immediately the important problem arises as to what extent such intercollegiate comparisons can be made and how closely the test results expressed in the percentile norms will coincide with an individual instructor's appraisal of a particular student.

The present study has been undertaken in a four-year liberal arts women's college over a number of years,

[1] Chemistry tests, obtainable from the Examinations Committee, American Chemical Society, St. Louis University, St. Louis, Missouri.

and includes all members of the classes in qualitative and quantitative analysis. Each of these classes was in session for one semester (16 weeks of instruction: two 3-hour laboratory periods and two lecture-recitations per week). The classes were given five or six written 45-minute tests during a semester. About one-half of each test was devoted to newly presented material, while the other half reviewed the field. The tests were evaluated in letter grades, which were translated into percentiles later for the purpose of the study, setting—arbitrarily but according to usual practice—A at 100–90; B, 90–70; C, 70–30; D, 30–10; F, 10–0.

Figures 1 and 2 show the average grade received by each student plotted versus the percentile score made in the A. C. S. cooperative test, which was given as part of a final examination.

In a case of ideal correlation all the points in Figures 1 and 2 would fall on the diagonal line. Large deviations from the diagonal mean that the instructor has assigned a certain letter grade to the student but that the score on the A. C. S. cooperative test indicates a different letter grade. For certain small deviations from ideality the letter-grade limits may not be overstepped. These limits are indicated in Figures 1 and 2 by the two bell-shaped curves on each side of the diagonal line. In other words, we assume that a student's grade is determined by the instructor with a precision of one-half of a letter grade, a precision of ±5 per cent on abscissa and ordinate for A, ±10 per cent for B, and so on. Of a total of 104 points in Figures 1 and 2, only 13 points are outside these precision limits and an 87 per cent correlation can be concluded.

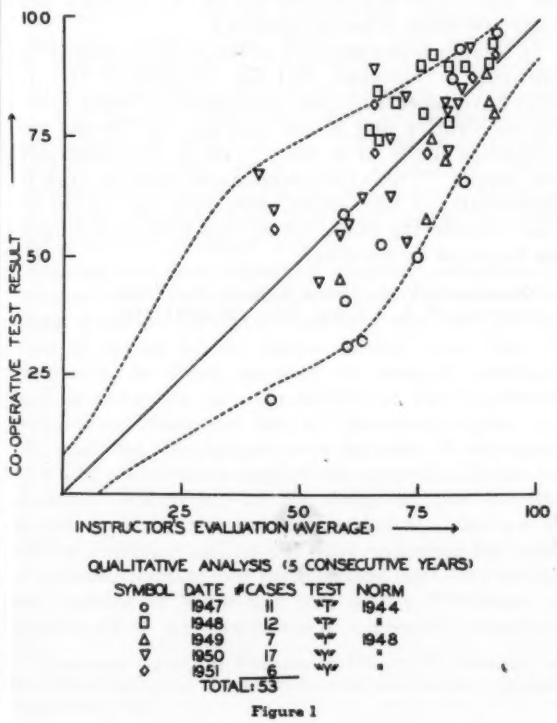


Figure 1

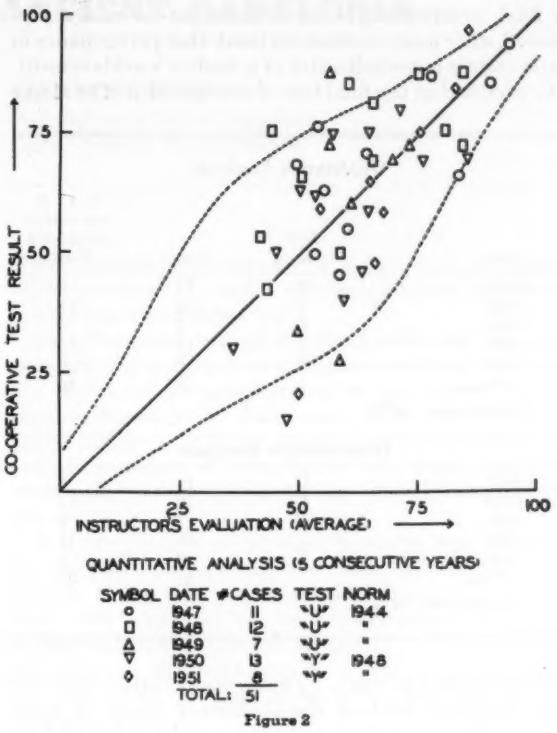


Figure 2

A more individual comparison between the A. C. S. cooperative test results and the instructor's appraisal can be attempted from the following considerations: suppose student R received during a semester the following marks: B−, B+, B, B+, B+ (average 77 per cent); while student M showed C, C, C+, B−, B−, A− (average 65 per cent). In the former case we would be fairly justified in thinking that any other test would bring a result close to 77 per cent and the same prediction should hold true for the A. C. S. cooperative test. In the case of student M the result in

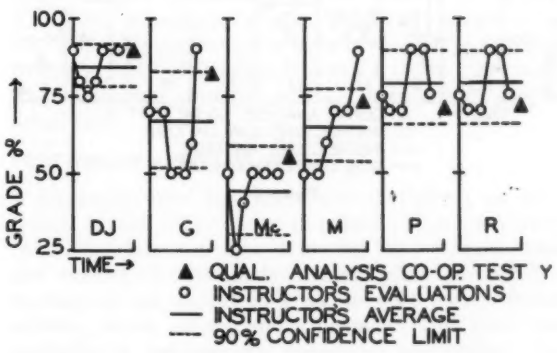


Figure 3

a final, comprehensive test cannot be so easily predicted, since many instructors think that performance in later tests is more indicative of a student's achievement. We expect that the final test of student M will be above the 65 per cent average. These considerations lead into the statistical field of the confidence limits of averages. These confidence limits can be computed as $\pm ts/\sqrt{n}$, where t is obtained from tables or nomographs,[2] while s is the optimum standard deviation estimate or $\sqrt{\sum d^2/n-1}$, where n is the number of observations and d is the deviation of an observation from the average.

Qualitative Analysis

Year	*Test no.*	*Cases*	*A. C. S. test within confidence limits*
1947	*T*	11	8
1948	*T*	12	11
1949	*Y*	7	6
1950	*Y*	17	15
1951	*Y*	6	6
TOTAL		53	46

Correlation: 87%

Quantitative Analysis

1947	*U*	11	8
1948	*U*	12	11
1949	*U*	7	5
1950	*Y*	13	11
1951	*Y*	8	6
TOTAL		51	41

Correlation: 81%.

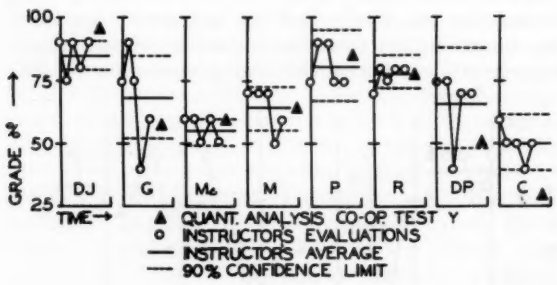


Figure 4

Figures 3 and 4 show test results for 1951 classes. The plot also contains the averages and 90 per cent confidence limits of the averages. In the case of the above-mentioned student R (see quantitative analysis class, Figure 4) there are nine chances out of ten, according to the statistical computation, that in any number of tests the average result will be within the limits 77 ±4 per cent or within the brackets of 73 to 81. Similarly, for student M we are now 90 per cent confident that the average would be between the limits 65 ±12 per cent (see qualitative analysis class, Figure 3).

Since we have about three times more precise information regarding student R than we have on M, we should be more rigorous in comparing the cooperative test result with this student's grade average.

The 90 per cent confidence limits of the averages were therefore computed for all of the 104 observed cases, and the findings are reported in the table.

In a total of 104 cases the cooperative test result was 87 times within the expected limits, indicating an 84 per cent correlation. This is exceptionally good and about as much as could be expected, for two reasons: first, the cooperative tests attempt to measure the material "common" to all the courses throughout the country. The "uniqueness" of each course is, of necessity, ignored. Second, the tests are limited to recognition-type items and do not measure all the endeavors of instruction. The Committee recommends that the instructors supplement the A. C. S. tests with essay and other types of problem.[3]

In this study two methods of comparison between the instructor's evaluation and the cooperative test results have been used, the letter-grade average versus the cooperative test results and also the 90 per cent confidence limits of averages versus the cooperative test results. These two comparisons seem to work independently of each other, since over one-half of the cases outside the limits set by one method are inside the limits set by the other.

[2] NEKRASOFF, V. A., *Metron*, **8**, No. 3, 95–9 (1930).
[3] ASHFORD, T. A., J. CHEM. EDUC., **25**, 280 (1948).

PERFUMERY IN ANCIENT BABYLONIA

MARTIN LEVEY
Pennsylvania State University,
State College, Pennsylvania

Our knowledge of the history of Babylonian chemistry is derived from two main categories of evidence, the first being the artifacts of the ancient civilizations unearthed in this region, and the second being literature of this period which has been recovered. The latter includes the study of the level of Egyptian science and that of other districts which were in contact with Babylonian learning and culture. Most important of the less direct avenues of approach to the study of ancient Babylonian chemistry is the manner of transmission of the science and its status in the later Greek and Moslem civilizations.

Babylonian chemistry of the second millenium was an applied science. It had been developed on an empirical basis, through the countless experiments and practices of daily living, from prehistoric times. At the same time, nevertheless, this chemical branch of technology had a number of genuinely scientific elements implicit in its techniques and procedures.

HISTORICAL SOURCES

Until now our knowledge of the history of ancient chemistry in the written sources has come primarily from the glass-making texts of the seventeenth (*1*) and seventh (*2*) centuries B.C. The former text is of a cryptic nature so that its complete understanding will have to await our fuller acquaintance with the technology of the period. The latter texts have yielded information of a more substantial nature including the various chemicals utilized in glass making and glazes, the fuel used, and clues for the construction of high-temperature furnaces.

One of the most important chemical industries in Babylonia was the preparation of aromatic substances. These products had four main uses reaching into the lives of almost all the people in the Near East: in medicines, in ritual services, in magical practices, and in cosmetics (*3*). In tablets of the nineteenth century B.C. there are lists of therapeutic spices (*4*). Although the Babylonians were ignorant of antisepsis, they did nevertheless employ the essential oils for infections. Waterman, in his study of the Assyrian period, came to the conclusion that "...the use of oils for anointing against the wind, of lotions for fever, of external applications for infection, and sore throat, and bathing of hands and feet with a distillation of lidrusha plant, and cassia, aim at a scientific procedure. Other medicaments consist of a 'plant of sickness,' oil of ironwood (?), and a concoction made by boiling a sihhi plant with beryl." (*5*).

In a Sumerian text of the third millenium B.C. the essential oils and aqueous extracts containing these oils are employed in prescriptions in this oldest known medical document of Babylonia. Thus the Sumerian tablet implies that these people were acquainted with various processes of extraction of oils from botanicals 1000 years before the Akkadian tablets discussed in this paper (*6*).

A vast quantity of perfume products was required for religious purposes in the form of essential oils, waters of perfume, and salves. Herodotus relates that 1000 talents of incense were consumed annually in the Babylonian Temple of Bel (*7*). The ritual of the Hebrews also made use of incense, holy anointing oil, and other perfume products as described in the Old Testament (*8*).

The latest discovery to shed more light on the history of Babylonian chemistry is a group of tablets describing the manufacture of perfume products. Included in these, all written in Akkadian cuneiform, are two texts with recipes for perfume preparations and five texts dealing with the technological aspects of perfumery. One of the latter texts is said to have belonged to the library of Tiglath-Pileser I (1115–1089 B.C.); the remaining tablets, from the inscription on one and their similarity in style and content, all date from the reign of Tukulti-Ninurta I (1256–1209 B.C.). Their chemical contents will be discussed in greater detail later.

PERFUMERY APPARATUS

Apparatus used by Babylonian perfumers, as mentioned in the texts under discussion, was completely of the kitchen variety. Included were various sizes and shapes of pots made of clay, glass, or metal, a measuring cup (equal to 1 qa, or 0.41 liters), flasks, stirrers, bowls, sieves, and a furnace. One piece was probably a sublimatory apparatus resembling that utilized by the later alchemists. It may be supposed to have consisted of a pot with a wide lip having a trough so as to catch the sublimed liquid dripping down from the lid. Strong evidence for the use of this apparatus is also to be found in works of the later Alexandrian chemists. The liquid was then soaked up with a cloth and the operation continually repeated. Extensive use of cookroom apparatus is not very surprising since two women, by name Tappûti-Bēlatēkallim,

[1] Presented before the Division of History of Chemistry at the 124th Meeting of the American Chemical Society, Chicago, September, 1953.

the Perfumeress, and (—)nīnu, the Perfumeress, are cited in their respective texts. The early history of chemistry is thus indebted to these second-millenium women as well as to their feminine successors in the early centuries of the Christian Era in the persons of Mary the Jewess, Paphnutia the Virgin, Cleopatra the Alchemist, and Theosebeia, the sister of Zosimos.

The methods used for the winning of perfume in the Babylonian literature are reflected, almost in their entirety, in a ninth century A.D. work on perfume chemistry by al-Kindī (*9*). The one important exception is that by al-Kindī's time distillation was in widespread use and so it occupies a prominent position in his book. In the Babylonian texts there are descriptions of extractions using oil, water, or both together as vehicles and the possible use of sublimation as a form of distillation.

In the following passage, a description of the use of expression followed by extraction with oil is given as a procedural step in the manufacture of perfume.

> On the fourth time of pouring together, you heat fresh good well water and pour it into a hirsu pot; then you pour $^1/_2$ qa calamus, $^1/_2$ qa myrrh, expressed and filtered, on the heated water in the hirsu pot. The mixture stands overnight and is steeped. In the morning, you filter the water and aromatic, using a cloth sieve, into another hirsu pot. Remove the dregs. Then you measure 3 qa calamus, 3 qa expressed, filtered myrrh, and 40 qa water which had been overnight with the calamus and myrrh and do as was done earlier with the calamus and myrrh. Light the fire. When the water necessary for the mixture is heated, pour in the oil and stir. When the oil, water, and aromatic penetrate one another, you need not shake it further. Cut down the fire under the diqaru pot and let it stand for two or three days. . . . (*10*).

It is interesting that in this procedure the water of perfume of the first steeping process is used for the second batch in the following steeping step. In Babylonia the usual technique in the derivation of the perfumes from plant materials consisted of approximately twenty tedious and painstaking steps, each comprised of a number of subsidiary operations.

As has already been mentioned, the Babylonian perfume texts give strong evidence that the process of sublimation was utilized. That the evidence is incomplete is a result both of lacunae in the texts and of their highly abbreviated character. Campbell Thompson has shown that sublimation was practiced in Babylonia, particularly in metallurgical processes. It would be difficult to believe that the Babylonians, who were acute observers, were not aware of the so-called heavier oxide of zinc, and the pompholyx, or lighter oxide adhering to the upper part of the furnace (*11*). There is also philological evidence that the "sublimate of the red" from cinnabar, as well as sal-ammoniac, were known as sublimates (*12*). The latter was prepared from the soot of dung fires, in the same way that it was obtained in later times by the Moslems and Indians.

The evidence for sublimation is given in the following quotation from one of the perfume texts:

> On the tenth pouring together, remove the oil, and heat the water gently. Wash a hariu pot and pour into it 2 beakers of balsam condensate and let it stand all day. In the evening place the water of the hariu pot and 13 qa of balsam in a bowl and let stand overnight. Kindle the fire and let the aromatic get hot. Pour oil into the diqaru pot, stir, and cover. Do not remove the organic material. The fire will become intense and the oil will throw up foam. The betanu [trough in the lip] of the diqaru pot you will repeatedly wipe up with a handcloth. You stir and cover and it remains four days in its diqaru pot. The next morning you will kindle a gentle fire (*13*).

The balsam condensate mentioned is the product derived from the previous operation and serves as a vehicle for the 13 qa of (comminuted) balsam to which more oil is later added. This resembles the medieval process of cohobation. In present-day distillation the aqueous layer in the receiver is pumped back into the retort automatically since it contains not only dissolved volatile oil but also oil in emulsified and suspended forms, the quantity depending on solubility and specific gravity of the various oil constituents. The technical requirements of sublimation as apparently used by the Babylonians necessitated considerable experience. Much more difficult than steam distillation or the combined steam and water method, hydrodistillation of essential oils, which resembles the sublimation method more closely and is in use in some parts of the world today, is a very complex procedure requiring much knowledge of its variations (*14*).

The yields of the Babylonian chemists must certainly have been very low with many impurities present, such as decomposition products in the nonvolatile plant constituents (methyl alcohol, formaldehyde, acetaldehyde, acetone, low fatty acids, nitrogenous compounds, phenols, etc. (*15*) and polymerized aldehydes. In addition, the yield was lowered by partial hydrolysis of valuable esters such as linalyl acetate.

The perfume texts also describe the preparation of perfume water by means of forty extractions of balsam extract with water. This is strongly reminiscent of the many different types of repetitive operations performed by the Alexandrian and Arabic alchemists. For the Babylonian chemist, repetition of chemical operations was absolutely essential for a greater yield. But for later Greek and Arabic workers, with distillation in common usage, there was much less need of repetition. However, under the strong hand of tradition originating in Babylonia the alchemists retained the old procedure in spite of later technical advances.

Two of the tablets are concerned with perfume recipes. These detail the amounts of the constituents making up the final product. This is of interest since in the medical and pharmacological Sumerian and Akkadian texts mention is rarely made of the amounts of simples used in prescriptions. This was done to maintain the secrecy of the medical guild for the protection of its members. Regarding the chemical documents, in spite of the fact that quantitative measures are given, not very much is divulged owing to the difficulty of the various chemical operations.

The newly described second-millenium texts on perfume chemistry giving the preparation of perfumes,

perfume water, and aromatic salve will prove of the greatest importance to our knowledge of the history of ancient chemistry. In addition to being the oldest texts giving such full elaboration of chemical methods, they are objective, descriptive directions without the least bit of magical, mystic or cryptic influence. It is true that Babylonian chemistry as described in the texts is but technological in scope. However, it was Babylonian applied chemistry which built up the strong base of empirical knowledge upon which later chemists were to erect the foundations of our present chemical science.

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(4) GOUCHER, II, 249; also II, 258, 358.
(5) WATERMAN, L., "Royal Correspondence of the Assyrian Empire," Part IV, 35. *Cf.* DYSON, G. M., "Physiological aspects of the essential oils," *Perfumery and Essential Oil Record, Special*, No. **21**, 287 (1930).
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(7) HERODOTUS, I, 183.
(8) See, *e. g.*, Exodus 30: 23–4; II Chron. 16: 14; Exodus 30: 1–7.
(9) GARBERS, K., Editor and Translator, "Kitāb Kīmiyā' Al'-Itr Wat-tas'idat von Ya'qub B. Ishāq Al-Kindī," *Abhandlungen für die Kunde des Morganländes*, **30**, Leipzig, 1948.
(10) Free translation utilizing EBELING's transliteration, *op. cit.*, pp. 29, 30.
(11) CAMPBELL THOMPSON, R., "A Dictionary of Assyrian Chemistry and Geology," Oxford, **1936**, p. xx.
(12) *Ibid.*, pp. 23–30.
(13) EBELING, *op. cit.*, 18–20.
(14) GUENTHER, E., "The Essential Oils," D. Van Nostrand Co., Inc., New York, **1948**, Vol. I, p. 145.
(15) *Ibid.*, p. 156.

AN OXIDATION-REDUCTION DIAGRAM

ALEXANDRE R. TARSEY
Titanium Metals Corporation of America,
Henderson, Nevada

THERE is an adage that one picture is worth a thousand words. It applies well to chemistry. Thus there is still a general interest in slight rearrangements of the periodic chart, although that chart is well understood in principle.

Similarly, a visual approach will help in correlating the various concepts pertaining to oxidation and reduction potentials. The following is the description of a chart which may serve that purpose, inasmuch as it brings forth a graphical representation of a number of interesting relationships.

CONSTRUCTION OF CHART

An example of the chart is shown in Figure 1, which represents the elements of Group I-B. Similar charts can be made for other groups or individual elements.

The X-axis represents the various oxidation states. The lines from the point representing the elemental states to the points representing the +1 states are drawn so that their slopes are equal to the half-cell potentials of the M^0–M^{+1} couples. Similarly, the lines connecting the +1 and +2 states of each element show by their slopes the oxidation potentials of these couples.

The Y-axis was then graduated using $^1/_{23.066}$ times the scale of the X-axis, as shown on the left margin of Figure 1. It was furthermore graduated on the right margin at $^1/_{17}$ or 0.059 times the scale of the X-axis.

PROPERTIES

This chart will show the E^0 of *any* half-cell by the slope of the line connecting the couple. This is true not only for the lines with which the chart was constructed, but for any line that is drawn between two points representing oxidation states of an element. Thus a line connecting Cu^0 and CuO^{+1} would show the oxidation potential of that half-cell, and would demonstrate why this potential is not the sum of the Cu^0–Cu^{+2} and the Cu^{+2}–CuO^{+1} couples, but rather a weighed average of the two, *i. e.*, the slope of the vector sum.

Another property of this chart follows from the Nernst equation: that the ΔF, in calories, of *any* half-cell can be seen as the difference of the Y-coordinates of the couple, using the graduations on the left margin of the chart.

This chart should furthermore eliminate any confusion regarding the sign of the half-cell potential. Any "uphill" reaction is relatively difficult because of the necessary increase in free energy, whereas "downhill" reactions will tend to occur the more readily, the steeper the path.

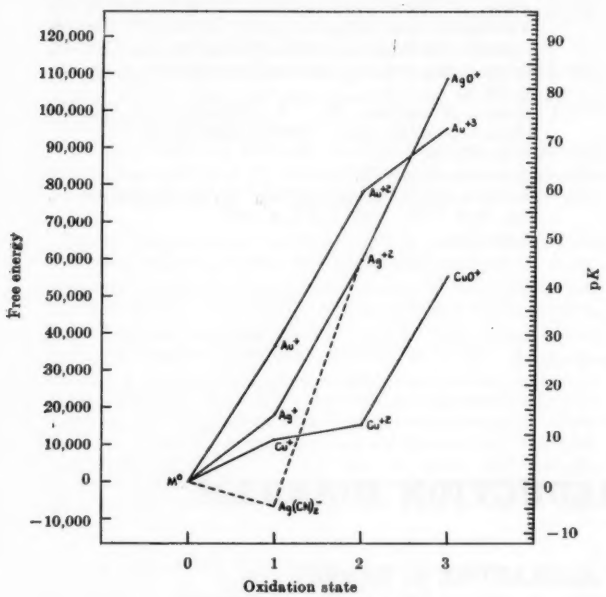


Figure 1. Group I-B

One of the most important properties of this chart, which is not readily brought forth by other means, is its indication of the relative stability of the various oxidation states. Now it is obvious and needs no graph to expound that metallic gold is less readily oxidized than metallic copper. That follows from the numerical values of their oxidation potentials—if the sign convention is given. But the chart goes further. Look at the copper curve. Any e. m. f. powerful enough to push Cu^0 up the steep step to the +1 state is sufficiently powerful to continue the oxidation to a higher state, since there is a crestlike break in the curve at the +1 state. The opposite is true of Cu^{+2} which is located at a very definite concave break in the curve. Cu^{+2} is therefore quite stable!

The chart thus not only shows the various known oxidation states of each element, but shows also which ones must be the most common. Thus the +2 state of copper, being in a crevice, is a common oxidation state of that metal, as must be the +1 state of silver, even though the latter is seen to be easily reduced. As for gold, we see not only that it is difficult to oxidize, but also that the +2 state is very unstable, and that even the +1 state is not particularly stable since it is not in a crevice. As a matter of fact, Au^{+1} will be located on a slight crest when the straight line from Au^{+1} to Au^{+3} is drawn in, and can thus undergo autoxidation to the latter state.

Furthermore, the chart can bring out periodic relationships. Thus with increasing atomic number the metals of this group become more noble, which is another way of saying that in solution it becomes more difficult to achieve some higher oxidation state. A study of Figure 1 will show that for Group I-B an increase in atomic number results in somewhat of an increase in the stability of the +1 state, in a definite decrease in the stability of the +2 state, and in a definite increase in the stability of the +3 state.

It must be kept in mind that ordinary electromotive series are either mere lists of the reactivity of some elements in some particular solution, such as 0.1 *N* HCl, or else lists of the E^0's of the most important couples. Similarly, the diagrams discussed so far are limited in that they are constructed by the use of E^0's, representing behavior in solutions so strongly acidic that the hydrogen ion activity is 1.0 *N*.

When this limitation is not serious, these charts should be used as they are for the sake of simplicity. Nevertheless, it may become desirable to study the effect of a change in conditions. Now a change in hydrogen ion concentration does not change the positions of the points representing either simple monoatomic ions or the elemental states, their half-cell potential not being affected. What do change are the "critical slopes" at which couples may begin to liberate hydrogen from the solution, and those at the substance itself may be reduced by the process of liberating oxygen. These slopes are shown in Figure 2. (The reader need not be reminded that when the element in question is a metal, an increase in the hydroxyl ion concentration in the presence of an oxidized state may often result in exceeding the solubility product of the hydroxide.)

Ions which do contain oxygen, such as CuO^{+1}, will change their position on the chart with a change in pH, since the formation of such ions becomes less difficult when there are fewer hydrogen ions competing for the oxygen. The new location of such ions is readily predicted: an increase in pH from 0 to 14 results in a stabilization as indicated by a shift down the Y-axis of the chart through a distance corresponding to 38,000 calories for each atom of oxygen per atom of the element. This value is the difference in free energy between the reactions

$$2OH^- \rightarrow H_2O + O^{--}$$

and

$$H_2O \rightarrow 2H^+ + O^{--}$$

Another method of stabilizing oxidation states is the formation of complex ions. Such stabilization would again be represented by locating the complex ion on the chart below the corresponding ion of the

element in question at a distance representing the decrease in free energy. Thus the $Ag(CN)_2^-$ ion may be located in Figure 1 at a distance of −24,670 calories from the Ag^{+1} ion, this value being its free energy of formation from the monovalent silver ion and aqueous cyanide ions. The potential of various couples involving this complex ion will then be represented on the chart by the slope of straight lines which can be drawn to this new point.

Rules governing the stabilization of oxidation states by the formation of insoluble compounds are readily arrived at by analogous considerations.

There is yet another relationship brought out by this type of chart: that between concentration at equilibrium and the other values mentioned so far. Negative logarithms of equilibrium constants, or pK's, may thus be read as differences of Y-coordinates on the right-hand margin of the chart, just as the corresponding differences in free energy may be read on the left-hand margin. Figure 1, for example, shows that Ag^+ will be reduced to metallic silver by gaseous hydrogen in normal acid solution until the concentration is about 10^{-13} N. It also shows that the corresponding equilibrium value for gold is only 10^{-28}, and that the reduction of Au^+ by metallic silver must cease when

$$\frac{[Au^+]}{[Ag^+]} = 10^{-15}$$

It follows that a particular ion may be located on the chart when either an E^0, a ΔF, or an equilibrium constant is known. That is perhaps the chart's most instructive property. Thus we have already located the $Ag(CN)_2^-$ ion below the Ag^+ ion by the knowledge of the free energy of formation. The graph now shows that the half-cell potential of the Ag^0–$Ag(CN)_2^-$ couple must be 0.29 volt, and that the instability constant of the complex is about 10^{-18}. The knowledge of any one of these values would have been sufficient, of course, to locate graphically the stabilized ion.

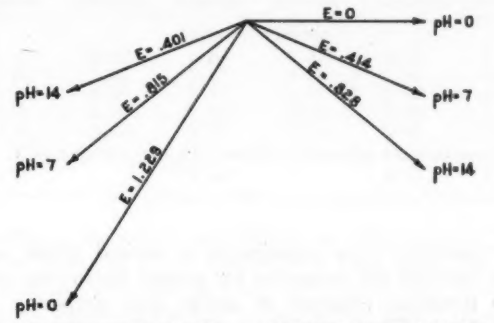


Figure 2. Critical Slopes

In conclusion, it should be mentioned that the numerical values used were taken from Latimer's oxidation potentials,[1] wherein may be found an extensive collection of such data published prior to 1938.

[1] LATIMER, W. L., "The Oxidation States of the Elements and Their Potential in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938.

"CONTRIBUTIONS TO THERMODYNAMICS: THE ANOMALOUS HEAT OF VAPORIZATION OF HEPTANE," BY J. McQUIRG

WORDEN WARING
Arthur D. Little, Inc., Cambridge, Massachusetts

IN HIS paper on "The anomalous heat of vaporization of heptane,"[1] Dr. McQuirg takes some excellent data and perfectly valid thermodynamic equations and manhandles them to produce very misleading results. His method of fitting a three-parameter equation by choosing three points is inefficient at best; here it leads to quite erroneous conclusions. For he takes triplets of points quite close together, so that the experimental scatter is highly magnified. His point 1, for example, lies slightly above the general trend of the data; when it is used together with nearby points a greatly exaggerated slope of the curve is calculated. When the other points are chosen farther away, the slope is less exaggerated and approaches a legitimate representation. Dr. McQuirg could equally well have presented a thesis opposite to his present one by starting with a point below the general trend of the data. The behavior he presents is not a measure of the behavior of the heat of vaporization (or the vapor pressure), but simply an indication that the statistical scatter of the data is beginning to be compensated for by the use of a longer "base line" for fitting the curve.

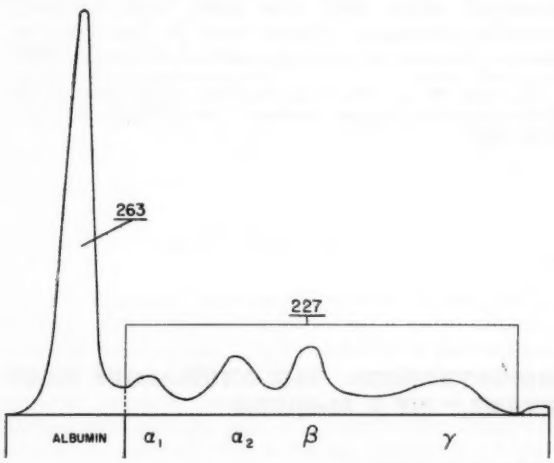
[1] For the article that is discussed here, see page 347 of this issue.

COMPARATIVE ANALYSIS OF SERUM PROTEINS BY CHEMICAL AND ELECTROPHORETIC MEANS

An Experiment in Biochemistry

FABIAN LIONETTI and M. MOIRA DAVISON
Boston University School of Medicine,
Boston, Massachusetts

OCCASIONALLY an experiment is devised which not only satisfies the requisites for proper instruction but also possesses elegance of design and simplicity of execution. These attributes plus enthusiastic reception by the student add up to unusual success. The rapid expansion of knowledge of the physical and chemical properties of blood proteins demands that the biochemical laboratory education include as many of the newer concepts as can be conveniently manipulated and assimilated by medical students with limited scientific training. Electrophoretic analysis of serum proteins by such students is hardly a practical problem to be attempted in a given week. However, during the past year we have aided our biochemistry class in accomplishing not only electrophoretic analysis of a given sample of serum but also chemical fractionation and analysis as well. Moreover, unexpectedly good correlations between physical and chemical methods were obtained in a majority of the 16 weeks of experimentation, and the experiment impressed the instructors as a most successful effort.



Pooled Human Serum

Ascending boundary, veronal buffer, pH 8.6, $\Gamma/2 = 0.1$.

"Total protein"	490
Albumin	263
Total globulins	227

$A/G = 263/227 = 1.16$

For this experiment, the class was divided into groups of five or six students. In outline, the experiment consisted of an orientation lecture on electrophoresis, demonstration of the instrument (Tiselius), interpretation of patterns, and presentation of photoprint copies on rectangular coordinate graph paper of the pattern for an experimental sample of pooled human serum. A graphic integration of the pattern curve was performed by each group, and the albumin-globulin ratio was computed. A sample of the same serum was then analyzed chemically by each group, the *A-G* ratio was determined, and results were compared with the electrophoretic value. Alpha, beta, and gamma fractions of the serum were similarly compared by the physical and the chemical method, although major emphasis was placed on the *A-G* ratio because of its diagnostic significance in routine clinical chemistry.

PROCEDURE

Preparation of Serum. Prior to the class exercise, human serum was prepared as follows. A hospital clinical chemistry laboratory collected the sera remaining after required analyses were performed, until the volume of the pool reached about 200 ml. The blood was obtained from patients suffering from a wide variety of diseases, many of which caused no change in the total protein content and some of which caused a hypoproteinemia. The pool was filtered through a D6 Steriflow filter (Hormann) and divided into 10-ml. portions. Precautions were taken to insure sterility of the samples, since it was desired to keep some at least four months. The serum was stored in 25-ml. sterile bottles at 1°C.

Electrophoretic Analysis. The serum was diluted 1:5 with veronal buffer at pH 8.6, $\Gamma/2 = 0.1$, and dialyzed against the same buffer for one week at 7°C., the external buffer solution being changed at appropriate intervals. The dialyzed material was resolved for 139 minutes in a 2-ml. cell, current = 6 ma. and potential drop = 117 volts. A four-fold magnification of the Philpot-Svensson lens pattern was mimeographed

on graph paper. By the method of weighing, the *A-G* ratio was estimated at 1.24; by the method of counting squares, at 1.16.

Electrophoresis Lecture. Each group of five students was given a one-hour informal lecture on the principles and uses of electrophoresis. The essential parts of the machine were described and a demonstration of the technique of filling the cell was given. The students were shown a wide variety of electrophoretic patterns, representing a monophasic system, multiphasic systems, normal and pathological human sera, and sera of various species. Graphs of pH versus mobility were shown to facilitate understanding of the isoelectric point. Each group was provided with a mimeographed pattern and directed to determine the *A-G* ratio by an optional graphical integration procedure and to correlate the value computed by this physical means with that obtained by chemical fractionation and analysis.

Chemical Determination of the Serum Proteins. A detailed procedure for fractionating the serum proteins into total protein, albumin + alpha globulin, gamma globulin, and beta globulin, and their determination with alkaline copper sulfate reagent (biuret) is given by Consolazio, *et al.*[1] The principle, apparatus required, reagents, procedure, sample calculations, and precautions are adequately described so that the student group, if provided with reagents, could individually accomplish the total procedure in four to six hours.

The total protein value of the pooled human serum was 6.60 grams per cent, as determined by the micro-Kjeldahl procedure followed by nesslerization (protein conversion factor, 6.25). A standard curve was prepared by using bovine serum albumin in increments of 0.01 mg. from 0.76 to 7.00 mg. albumin per 3 ml. of sample analyzed. Using this curve, analysis of the pooled serum measured 6.50 grams per cent by biuret technique. The curve was used weekly by each group after first verifying several points.

Calculation and Correlation with Electrophoresis. The chemical composition of the pooled serum sample determined by five representative groups of five students is given in the table. The composition computed by the group from the electrophoretic pattern of the same serum is illustrated in the figure. The area under the curve was most conveniently obtained by counting cross-section squares. In a surprising number of instances, the more painstaking student obtained good correlation of the physical and chemical methods. The most difficult part of the procedure was the determination of the albumin fraction, which required particular care in avoiding high results, because of contamination of the fraction with precipitated proteins. Since the total globulin was computed from the total protein value minus the albumin, a high value for the latter resulted in an exaggerated high value for the *A-G* ratio. Nevertheless, when such pitfalls were pointed out to the students, the results in the hands of inexperienced workers were often gratifying.

Comparative Analysis of Pooled Human Serum by Biuret and Electrophoresis

Total protein	*Albumin + alpha globulin*	*Albumin*	*Gamma globulin*	*Total globulin (T. protein − albumin)*	*A/G*
		(In grams/100 ml. plasma)			
		Chemical analysis			
6.50	4.83	3.63	0.91	2.87	1.26
6.64	5.27	3.67	0.78	2.97	1.24
6.16	4.50	3.17	0.99	2.99	1.06
6.66	5.83	3.66	0.83	3.00	1.22
6.14	4.65	3.67	0.88	2.47	1.48
		Electrophoretic analysis (method of counting squares) mm.[2]			
4.90		2.63		2.27	1.16

Popper, *et al.*,[2] made a detailed comparison of the electrophoretic technique with chemical analysis by the biuret method and found good correlations between the albumins, total globulins (and *A-G* ratio), the gamma globulins, and the beta + gamma (euglobulins) fractions. Poor correlations were found between alpha globulins and beta globulins. The 156 samples studied included 140 specimens from patients with liver disease and other disorders known to influence the serum proteins. It is possible to estimate the alpha and beta globulins from the measured quantities in the table, that is:

Serum alpha globulin =
(serum albumin + alpha globulin) − serum albumin

(Serum beta globulin + gamma globulin) =
total protein − (albumin + alpha globulin)

Serum beta globulin =
(serum beta + gamma globulin) − serum gamma globulin

However, errors in the measurements are too great to permit accurate determinations of these quantities by difference, and the student data were inadequate for this purpose. Nevertheless, the results derived were most gratifying in that the students were able to assimilate the rather formidable pedagogic concepts of electrophoresis, mobility, the isoelectric point, and chemical and physical fractionation of serum proteins in a surprisingly facile fashion. Much of this was accomplished by the expedients of actual manipulation and participation by the students.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Dr. Matthew A. Derow of the Department of Microbiology.

[1] Consolazio, C. F., R. E. Johnson, and E. Marek, "Metabolic Methods," C. V. Mosby Co., St. Louis, 1951, pp. 123–6.

[2] Popper, H., J. de la Huerga, M. Franklin, W. B. Bean, W. D. Paul, J. I. Routh, and F. Schaffner, *Am. J. Clin. Pathol.*, 20, 530–8 (1950).

TESTS FOR ALCOHOL IN BREATH AND BLOOD

JAMES M. BERKEBILE
McPherson College, McPherson, Kansas

A CRITICAL factor in law enforcement, attempting to keep intoxicated drivers off the highway, is to obtain conviction of the offender when he is apprehended. It is well known that many law violators escape the due penalty of law through the broad manner in which judges and juries interpret the visible evidences of intoxication. As a result there is a persistent and flagrant disregard for the law in this respect, culminating in a marked rise in highway fatalities due to drivers operating under the influence of alcohol.

Considerable research[1] has been conducted to determine the alcoholic content of body fluids with a view to correlating these values with the body reactions resulting in high accident rates on the highways. The alcohol content of the blood, breath, spinal fluid, urine, and saliva have been shown to give reliable measures of the amount of alcohol in the brain at the time the sample was taken. Standardized measures of relative body control at different concentrations of alcohol in the blood are now used in many states. The alcohol content of the breath, which is directly related to the alcohol content of the blood, is now easily obtained. A direct blood sample of the subject under question can be run in any ordinary analytical laboratory. This paper indicates two established procedures used for analysis of the breath and the blood. Most college laboratories are equipped to conduct the chemical analyses used in determining the alcohol content of either of these two body products.

Innumerable experiments have shown that the breath provides a very convenient, readily obtainable, and entirely reliable index of the alcoholic content of the blood.[1, 2] Results of these tests have now been accepted by courts across the land, even though specific legislation has not been enacted to provide for them. The McPherson city and McPherson County law enforcement officers have used the "Intoximeter"[3] and blood-sample method for almost one year; and where a state of intoxication has been indicated by the standardized values, not one case in court has been lost. The intoximeter is a device simple in construction, convenient to carry in the pocket of an overcoat or jacket, and can be operated by any person who has had a demonstration of its assembly and use. A diagrammatic sketch is given for the assembled device. The court record before this time was not too favorable, owing to the usual uncertain methods of interpreting the objective symptoms of intoxication. One great value has been the immediate release of drivers by the officers where the Intoximeter test gave no evidence of the subject's being under the influence of alcohol. Other charges, usually of lesser import, are made where evidence warrants it.

Where legislation has been adopted, such as in Maine, Indiana, Oregon, and New York, the following pattern is followed. Zone I: Where concentrations of 0.05 per cent or less alcohol are found in the blood there is *prima facie* evidence that the driver is not under the influence, even though the studies indicate this favors the offender. Zone II: Where concentrations are from 0.05 to 0.15 per cent the evidence is considered relevant but not *prima facie* evidence that the driver was under the influence. A few of those having blood alcohol slightly above 0.05 per cent will be affected. Near 0.15 per cent all will be affected. Zone III: An alcohol concentration in the blood of 0.15 per cent or above is regarded as *prima facie* evidence that the driver was definitely intoxicated.

The National Safety Council Committee on Tests for Intoxication[4] reports experiments demonstrating that abstainers and moderate drinkers show the influence of alcohol before a concentration of 0.05 per cent is reached; even heavy drinkers, possessing the greatest tolerance to alcohol, show influence at concentrations between 0.07 and 0.09 per cent. Many authorities consider 0.10 per cent concentration the upper limit of the range of zone II. In the experience of the author, court reports of the objective symptoms indicating intoxication would bear out the validity of the 0.10 to 0.11 per cent upper limit for zone II.

In using the convenient Intoximeter, the cardboard carton is opened and the train assembled. The person under question blows several liters of air, through the mouthpiece, *E*, and the valve, *D*, into the balloon furnished with the equipment. The balloon, *B*, is then connected to the device as shown in the sketch, and a portion of the breath-sample is allowed to flow through the glass cylinder containing an analytically determined amount of acidified potassium permanganate solution. The exact number of seconds required for the permanganate solution to decolorize, with the

[1] FORRESTER, G. C., "The Use of Chemical Tests for Alcohol in Traffic Law Enforcement," Charles C Thomas, Springfield, Illinois, 1950.

[2] Private communication from Dr. C. W. Muehlberger, Michigan Department of Health, Crime Detection Laboratories, Lansing 4, Michigan.

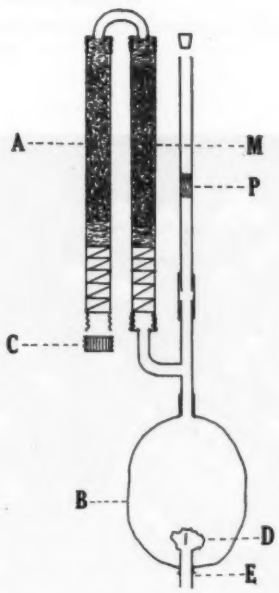
[3] Patented device by Dr. Glenn C. Forrester, Intoximeter Association, Niagara Falls, New York.

[4] National Safety Council: Committee on Tests for Intoxication Reports for 1938–41 and their appended references.

breath-sample flowing through it, gives the officer an immediate estimate of the state of intoxication. If the number of seconds required is 30 or less the man is undoubtedly under the influence. If the time required is more than 80 seconds the officer can rest assured that the difficulty is not due to a state of intoxication. The permanganate solution is retained in the fritted glass area labeled *P*. To retain a permanent record of the breath-sample the remainder of the breath is allowed to flow through the chemical train by removing the cap, *C*, on the Ascarite tube. Tube *M* contains pure magnesium perchlorate which takes up all the water and alcohol in the breath-sample. The previously weighed tube *A* contains Ascarite which removes the carbon dioxide of the same sample. It is customary for law enforcement officers to have the chemist weigh all Ascarite bulbs before the Intoximeters are used. They are then repacked and sealed for the officers. If this is not done, the only reliable record of the case is the observation of the officer on the time of the oxidation by the permanganate solution. If the chemist's analysis on the exact percentage of alcohol is desired for court proceedings the used Intoximeter is submitted for determination of the alcohol and carbon dioxide content of the breath-sample.

The weight of the carbon dioxide in the breath-sample is determined by reweighing the Ascarite tube after use. An analytical balance is used for this purpose. The amount of alcohol in the magnesium perchlorate tube is determined as follows: The perchlorate is washed from the tube into a 250-ml. round-bottom flask with approximately 50 ml. of water. Distillation of the sample is conducted in a distillation apparatus equipped with ground-glass joints. The receiver is a 25-ml. graduated flask. Approximately 25 ml. of distillate is collected at a moderate rate of distillation. All alcohol has been shown[5] to be removed from the dense salt solution with this quantity of distillate. A few drops of water are added to bring the volume of the flask to exactly 25 ml. Ten-milliliter samples are removed and oxidized with an excess of standard potassium dichromate in a hot acid medium. Back titration of the cooled diluted sample is conducted with sodium thiosulfate in the presence of an excess of KI using starch as an indicator. The amount of alcohol is determined in the 10-ml. sample by calculation. This value multiplied by two and one-half will give the total amount of alcohol present in the breath-sample.

To determine the percentage of alcohol in the blood one bases his calculations on the following reasoning: According to Henry's law the concentration of alcohol vapor in the alveolar air deep in the lungs is proportional to its concentration in the pulmonary blood. Alveolar air also has a constant content of carbon dioxide in the adult, approximately 5.5 per cent by volume. Therefore, if a sample of alveolar air is available for analysis the concentration of the alcohol in the blood can be (indirectly) determined. Even though exhaled air from the lungs is not alveolar air, the air which has not been deep in the lungs has picked up neither alcohol vapors nor carbon dioxide from the blood. However, the ratio of alcohol to carbon dioxide remains the same. From the calculation of the carbon dioxide content of the breath, the relative proportion of alveolar air can be determined. Then from the quantity of carbon dioxide in the breath-sample and the amount of alcohol in the same sample the per cent of alcohol in the blood can be determined. Analyses of both breath, by Intoximeter, and blood taken at the same time indicate a correlation within 0.01 per cent between the direct and indirect methods.



It has been shown that 0.2 g. of carbon dioxide, equivalent to 2000 ml. of alveolar air, also expresses the percentage by weight of alcohol in the blood. Thus the calculation of the percentage of blood alcohol is obtained as follows:

$$\% \text{ blood alcohol} = \frac{\text{wt. alcohol in the total breath-sample} \times 100}{\text{wt. } CO_2 \text{ in the total breath-sample} \div 0.200}$$

Thus the exact percentage alcohol in the blood can be determined in order to substantiate the charges of officers or to indicate that the charge was erroneous on the basis of established standards. This serves as a protection to the innocent as well as holding the guilty to a strict account.

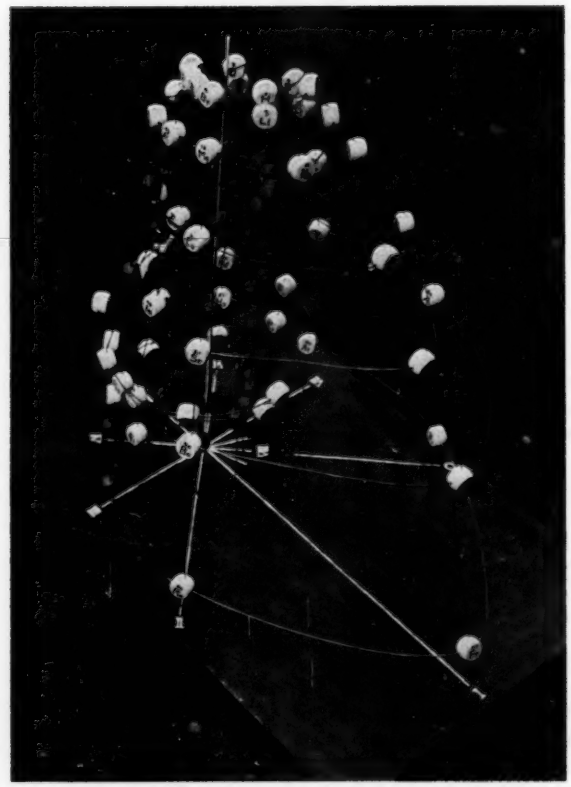
If one receives a blood sample, which any physician or nurse can obtain, it is quite simple to use a modification of the procedure given above to get the alcoholic content. Approximately 2 g. of blood accurately weighed is transferred to a 500-ml. flask with about 50 ml. of water. Ten grams of mercuric sulfate is added to reduce foaming. The collection and oxidation

[5] See footnote 2.

of the distillate are the same procedures as those used for the breath sample. The calculation of the percentage of alcohol is quite easy:

$$\% \text{ blood alcohol} = \frac{\text{wt. of alcohol in total blood sample} \times 100}{\text{wt. of blood used}}$$

If law enforcement officers have the assistance of college personnel near by, it paves the way for easier and more rapid indictment of the guilty and release of the innocent. It would seem reasonable that chemists who are interested in contributing to the community welfare would find familiarization with these and like procedures valuable. Community education to the use of precise measures for intoxication, and the contribution of our time in a professional capacity for service to our society are obligations we should not avoid.



A NEW SPACE MODEL OF THE PERIODIC SYSTEM OF ELEMENTS

S. HORIE
Tokushima Technical High School, Tokushima, Japan

VARIOUS attempts to represent the periodic system of the elements have been proposed, including several space models.[1, 2]

The space model of the periodic system here presented is characterized by taking atomic weight on a vertical axis and atomic volume[3, 4, 5] as horizontal distance from the axis. The unit in atomic weight measures 2 mm. downward from the top along the axis, and that in atomic volume 5 mm. along the radius on which each element belongs.

A wire spiral is fastened to an upright iron support, which represents the vertical axis, set in a hardwood base. The model is 50 cm. high and its projection on the base is oval with the major axis 52 cm. long.

Wooden balls with two planed sides are strung on the wire to represent atoms, typical elements colored white and transitional ones red. The symbol of the element and its atomic number are placed on both planed sides of each ball. On the base the radii are numbered clockwise, 0 (VIII), I, II, III, IV, V, VI, and VII. Two short radii are inserted between 0–I and VII–0 to accommodate the first and third members of the triads.

It is noteworthy that the typical elements are situated on the external circumferences and the transitional ones on the internal ones, while the rare-earth elements are in between.

ACKNOWLEDGMENT

Thanks are expressed hereby to K. Mikita, principal of Tokushima Technical High School, and to the chemical staff of the Faculty of Engineering, Tokushima University, for their helpful advice.

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[3] KELLER, R. N., "The lanthanide contraction as a teaching aid," J. CHEM. EDUC., **28**, 312 (1951).

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Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

PLASTICS IN THE ELECTRONICS INDUSTRIES[1]

RALPH L. MONDANO
Raytheon Manufacturing Company, Lowell, Massachusetts

CIVILIZATION has passed through various "ages," such as the Stone, Bronze, and Iron Ages. A specific material to designate the present age poses a problem. However, to a plastics engineer, there is the strong feeling that this is the beginning of the "Plastics Era." The existence of limitless supplies of the basic elements, such as carbon, oxygen, hydrogen, nitrogen, and chlorine, from which all plastics, with minor exceptions, are composed, presents a challenge without boundaries.

However, a few black clouds hover. City dumps are littered with the bright-colored pieces of discarded plastic toys, tableware, and gadgets. These inferior abortive products threaten to poison the minds of consumers against plastics. This is a black mark that the molding division of the industry has put against itself and the entire plastic industry.

There is a need for the producers of raw materials to advertise the decided advantages of strength and long life of their specific plastics, and manufacturers of finished products should place the trademark of the plastic material itself as well as the molders' trademark on the finished products. Manufacturers such as Monsanto, du Pont, Dow Chemical, Koppers, Celanese, and Bakelite should take the leadership to make this possible. Superior compounds are available that would give the consumer a better product at only a slight increase in cost. A typical example of a more durable product that is manufactured for the hospital supply houses is the molded nylon drinking tumbler. Hospitals have found it economical to buy the more expensive but long-lasting nylon drinking containers rather than glass ones.

COMMERCIAL FORMS OF PLASTICS

A *plastic material* is one that is formed by heat or pressure, or both. It is an organic material, a product of a synthetic process, and a high polymer.

Plastic materials are available generally as liquids or as solid powders or granules. The use usually prescribes the form in which it is procured: phenol formaldehyde is available as a water-soluble liquid, as a viscous casting resin, and as a molding powder. The water-soluble liquid, for example, is used to impregnate wood veneers to make decorative laminates, the casting resins to make patterns and cores for use in the iron foundry, and the molding powder to mold items such as radio cabinets. Thermoplastic resins are usually available as polymers in powder or granular form. The liquid monomers of some thermoplastics such as styrene are also used. The lacquer industry has made extensive use of solutions of polymers.

Manufacture of synthetic resins usually involves information about the temperature, pressure, and the proper time for reaction. With phenol-formaldehyde resins the different types are mainly a result of the time that the phenol and formaldehyde react together, and if heated too long the resultant product is worthless.

Very few people are aware of the magnitude of synthetic resin production. In 1953 production was 2.6 billion pounds, double that of 1947 and more than 6 times that of 1942. By 1955 capacity will be between 3.8 billion and 4.7 billion pounds. Production machines for nonplastic materials are likewise increasing in capacity. Taking into consideration expected increases in population, the plastics industry will offer a 75 per cent plastics increase per capita as compared to 10 per cent for steel and 30 per cent for aluminum.

Like other new materials entering the electronics industry, every new plastic has to overcome resistance to its adoption. It is not uncommon to hear a competent engineer comment that the only sure fact about plastics is that they are no good. Usually this attitude is a result of a misapplication of a plastic with bitter consequences. Overzealous molders, anxious to build

[1] Abstract of an address presented at the joint meeting of the New England Association of Chemistry Teachers, the Eastern Association of Physics Teachers, and the New England Biological Association, Brandeis University, Waltham, Massachusetts, December 5, 1953.

sales but inexperienced in the electronics field, have pushed plastic materials onto engineers who lacked the proper background to evaluate their selections fully. Today, however, most electronics companies employ plastics engineers who are trained to evaluate the available plastic materials and to avoid high temperature breakdown, low temperature embrittlement, and unexpected dimensional changes.

THERMOSETTING RESINS

The electronics industry uses sizable quantities of molded parts made from thermoplastic and thermosetting resins. The main criterion for their selection is the temperature the product will encounter in service. Thermoplastic resins will soften, melt, and decompose on being heated to elevated temperatures. (Exceptions to this general rule are Kel-F and Teflon.) A thermosetting resin may soften at the same elevated temperature but will possess a large percentage of its original strength. Compression molders, injection molders, extruders, vacuum forming units, and laminating presses are used to shape plastics. Along with these machines many different kinds of processing equipment are used, such as preheaters, plastics grinders, coloring tumblers, plastics finishing machines, and engraving machines.

Phenol-formaldehyde compression-molding powders account for a large portion of the electronics plastics business. These thermosetting molding powders are available with various fillers. The selection of the plastic that has the optimum properties for a specific application requires careful consideration. Among the factors to consider are the size of the required piece, the operating temperatures, the inserts required for mountings, the wall thicknesses, aesthetic features, the cost, and the special chemical and electrical properties. A glass-fiber filler imparts exceptional strength even at elevated temperatures (350–400°F.), whereas fillers such as chopped cotton afford comparable physical properties but only at relatively low temperatures. Mica is used as a filler in plastic electric insulators because of low moisture absorption and high temperature resistance.

Phenolic molding compounds have made possible the relatively inexpensive manufacture of electronic components. The plastic jacket can surround an assembled electronic component and be molded in position. Examples are resistors, capacitors, tubes, tube mountings, and coil forms.

Because of continual dimensional changes and moisture absorption of the plastic jacket, electrical components made to close tolerances can be guaranteed only for short shelf life. In operation, the ambient temperatures as well as operating temperatures can contribute to changes in the specific characteristics because of the differential thermal expansion of the plastic and other items. The fragile nature of the assemblies sometimes makes it necessary to mold the plastic jacket at lower pressures and at higher temperatures than usual. Use of low molding pressures is undesirable, however, because the finished product possesses lower heat stability, lower strength, and a higher moisture absorption. The only difficulty with phenolic tube bases, on the other hand, is their lack of prolonged temperature resistance in normal radio and television receiver operations. Continual operating temperatures of about 400°F. can embrittle phenolic structures to such an extent that the strains resulting from temperature cycling can cause a fracture. A better high-temperature molding powder is being sought.

THERMOPLASTIC RESINS

Injection molding has made it possible to use thermoplastic materials, thus providing additional sources of plastics for the electronics industry. Small radio cabinets, knobs, and coil forms are examples of these less expensive, serviceable plastic items made from thermoplastics.

Polystyrene (the plastic used extensively for toys and decorative articles) and polyethylene (the waxy-appearing plastic often used for acid containers, wire coatings, and refrigerator ice-cube trays) have excellent electrical properties. Plexiglas, distinguished by its excellent transparency, Tenite II, the tough material commonly used for tool handles, and various forms of vinyls (the good, weather-resistant plastic commonly used in raincoat manufacture) have served in many instances where substitutes of a nonplastic nature were not available.

PLASTIC LAMINATES

A laminate can be defined as a combination of fabric or fibers and a bonding resin, usually in layer form, and is classified as either a high- or a low-pressure laminate. Various materials can be selected to obtain special chemical or electrical properties. A high-pressure laminate is one that utilizes resins requiring curing pressures in excess of 1000 pounds per square inch. A low-pressure laminate is one requiring molding pressures of less than 400 p. s. i. Some require only simple contact, that is, a pressure no greater than that resulting from the weight of the individual layers of the laminate.

Most high-pressure laminates are restricted to "primary forms" such as sheets and rods and to simple cross sections such as angles and channels. Some high-pressure laminates used for insulation and electrical-element mounting panels use cotton, linen, and glass fabrics as well as high-grade papers, usually in combination with phenolic or silicone resins, the choice being governed by the operating conditions and electrical requirements.

Low-pressure laminates lend themselves to the manufacture of complex shapes. Inexpensive molds that are fabricated from wood, plaster, plastics, or even waxes can be used. Today the manufacturers of plastic boats, automobile bodies, and canopies are using low-pressure laminating techniques.

Low-pressure laminates for the electronics industry must, for satisfactory operation, be void-free. Void-free laminates do not have the moisture absorption problems presented by entrapped air. These laminates can be made using a vacuum technique, wherein the air is removed under vacuum while the fabric, such as glass, cloth, linen, asbestos, or cotton is impregnated with a catalyzed liquid resin.

The resins selected for low-pressure laminating are the thermosetting epoxies (which are condensation products of epichlorohydrin and bisphenol-A) and the polyesters (which are condensation products of unsaturated dibasic acids and polyhydric alcohols or glycols).

Silicone-resin laminates have good electrical and high-temperature properties but exhibit relatively poor interlaminar strength even with the use of high-pressure molding. Low-pressure silicone molding resins are available, but to date are difficult to use with the vacuum techniques because the resin is inherently a solid dispersed in a solvent. This condition gives rise to incomplete wetting of the fabric by the resin and results in voids and very poor interlaminar strength.

APPLIED RESEARCH

The Plastics Laboratory of the Raytheon Manufacturing Company is not at this time engaged in problems concerning injection molding, compression molding, or the laminating of primary forms and shapes. Investigations are, however, being carried out to produce higher-temperature-resistant radomes for aircraft and better erosion-resistant coatings. Other studies of importance are the evaluation of irradiated plastics; the application of a low-pressure silicone laminating resin; the proper and useful application of the fluorocarbons, namely, Teflon and Kel-F; the preparation of casting resins with fillers for certain electrical properties, commonly referred to as "artificial dielectrics"; the production of superior printed circuits with respect to metal-to-laminate bonds; and the evaluation of casting and potting compounds capable of withstanding temperature extremes of −50 to 250°F. without deterioration or fracture.

RADAR DOMES

"Radomes" (radar domes) and "microwave windows" are terms commonly used in referring to antenna covers. The radome protects the critical and delicate antenna from corrosion and accumulation of dirt, snow, and ice. In aircraft the radome is usually designed to prevent drag and at the same time protects the microwave antenna and its components. In addition the radome must interfere as little as possible with transmission and reception of the radio waves.

The universal radome material is glass fabric or fibers combined with a low-pressure thermosetting binder such as the polyester or epoxy resins. Simple, small radomes of the thin and thick wall types are at present made of high-pressure laminates.

The double thin wall radomes are seldom used except where severe de-icing problems are encountered and air passages are required in the radome structure to circulate hot air.

The most widely used radome structure today is the sandwich, which affords an electrically acceptable, strong, light-weight structure. It consists of two strong, thin skins firmly bonded to a light-weight, relatively weak core material. The core and skin thicknesses vary according to the design requirements. The skins are usually fabricated of glass cloth bonded with a polyester resin.

Expanded rubber, foamed plastics, and fabricated core materials of resin-coated fabric having "honeycomb" or "waffle" impressions have been used very successfully. Radomes using expanded sheet stock and the fabricated core materials such as "honeycomb" and "waffle" can be made with low-cost tooling but high labor costs. These types of radomes possess poor physical tolerances because of the mechanical procedures required to assemble and cure the radome.

FOAMED-IN-PLACE PLASTICS

The most valuable of the core materials are the foamed-in-place resins, such as a saturated alkyd resin foamed with meta-tolylene diisocyanate. This process is a delicate one and requires a great deal of experience before satisfactory results can be obtained. In the foamed-in-place technique a material is foamed between two skins that are held firmly in position by a matched mold arrangement.

Plastics are foamed in three different ways: a chemical reaction between the constituents liberates a gas; a gas-forming powder is incorporated into the plastic, which is then heated; a gas is bubbled through the liquid plastic as it is being cured. Not all foamed plastics require heat for the final cure. Some are catalyzed so that room-temperature cures are possible.

Foamed-in-place resins are in their infancy, but to the plastics engineer this material has many applications. A recent 50 per cent price cut in meta-tolylene diisocyanate will further encourage the use of foamed-in-place resins.

FLUOROCARBONS

Fluorocarbons such as Teflon (a product of fluorine and carbon) and Kel-F (a product of fluorine, carbon, and chlorine) are now available. The relatively non-polar nature of these materials gives them a low dielectric constant and a low electrical loss. Polystyrene and polyethylene compare favorably with Kel-F and Teflon with respect to electrical performance but are quite inferior in high- and low-temperature resistance. Teflon is poor with respect to corona, which limits its use. The impossibility of obtaining a serviceable bond of Kel-F or Teflon to any other material is a second big drawback. With the exception of Teflon these four materials can be injection-molded. Teflon is peculiar in that it has a softening point at which it appears jelly-

like, but upon further heating it sublimates and liberates dangerous fluorine gas. Therefore it is compression-molded and requires special care.

The fluorocarbons are currently available as molding powders and spray coatings. The latter exhibit poor mechanical strength, are very poor under abrasive conditions, tend to be porous, and do not adhere to metals.

CASTING RESINS

The continual trend in electronics for greater sensitivity and closer tolerances of complicated electrical components has brought about a demand for a process to freeze the components in a protective rigid jacket with little or no pressure applied and a minimum of heat applied for cure. This demand has brought to the market many different types of room-temperature and oven-curing thermosetting resins.

Among the more common casting materials employed by the electronics industry are the polyesters, epoxies, phenolics, styrene, and copolymers of these materials. Of these the polyesters and epoxies with and without fillers offer a wide range of rigidity, strength, and electrical and chemical properties. They can be formulated to give a rigid or flexible cured product. Flame resistance, heat resistance, and a high-impact product can be obtained by incorporating the proper filler or fillers. Polyester casting shrinkages ranging as high as 15 per cent can be lessened by the use of fillers. This resin does not exhibit tenacious bonds to metal and its cure is inhibited by the presence of copper or its alloys.

The epoxies, on the other hand, exhibit good bonding properties to metals and have electrical properties comparable to the polyesters. A cure can be varied over a wide temperature range, from room temperature for some epoxies to an elevated temperature for the solid, hot-melt epoxies.

Phenolics have been replaced by the polyesters and epoxies as casting compounds for electrical components because of poor electrical properties and the inherent acidity that leads to corrosion of metals. Phenolics are generally troublesome because they liberate water during condensation to solids.

PRINTED CIRCUITS

Printed circuits that utilize a laminate, with either one or both sides clad with a metal foil such as copper, are finding their place in the electronics field. A carefully prepared metallic surface of a metal-faced laminate is chemically treated and "printed" through a negative by means of ultraviolet light. Washing and etching removes all but the desired exposed portions. Holes for terminals are drilled or punched and leads for electrical elements are soldered, usually by a hot-dip process, to give a completed printed circuit. The poor bond between metal and laminate is a frequent difficulty, but further development is under way to overcome this defect.

IRRADIATED PLASTICS

The latest development in the plastics field is the irradiation of thermoplastic resins to obtain improved chemical and physical properties with little or no change in electrical characteristics. This is brought about by causing increased cross linking, hitherto practically impossible for thermoplastic resins, by use of high-energy radiation that contains many times the energy necessary for the normal polymerizing process for thermosetting materials. With polyethylene, for example, irradiation causes breaking down of the single bond between the carbon and hydrogen, liberates the hydrogen, and allows a primary-bond cross linkage to form between carbons of different chains. The most successful irradiation experiments to date have been performed in nuclear reactors.

Plastics are well on the way to taking their place with metals, concrete, and wood as basic construction materials. They are not substitutes, but new materials, capable of performing tasks most suitable to their own nature.

To the Editor:

I was very much interested in the letter of M. W. Welch in the April issue of THIS JOURNAL. Thoughts along somewhat similar lines prompted me to initiate a series of workshops for science teachers in this area recently. While we were not concerned solely with chemistry, our experience has indicated that there is undoubtedly quite an opportunity for service along these lines.

Each workshop started with a lecture, supplemented by appropriate films. Following this general session the group broke up into small sections, each one of which was directed by a staff member whose Ph.D. training was in chemistry, geology, botany, zoology, ornithology, etc. The response was excellent. The March meeting attracted 70 teachers and the April meeting 85.

We expect to enlist the aid of our local American Chemical Society chapter in expanding this program next year. Our experience certainly indicates that Mr. Welch has suggested a very timely proposal concerning a valuable service that the A. C. S. may render.

DONALD S. ALLEN

STATE UNIVERSITY OF NEW YORK
STATE TEACHERS COLLEGE
NEW PALTZ, NEW YORK

To the Editor:

The method for collection of chlorine in my letter in THIS JOURNAL for January, 1954, can be extended to and is a significant improvement over the usual laboratory techniques for examining the properties of hydrogen sulfide.

First, as with chlorine, I collect hydrogen sulfide by water displacement. I can collect, without difficulty, a half dozen or more large test tubes full of the gas without the odors, up to this point, being perceptible in the demonstration room.

Second, I pour water to a depth of about one inch into one of the test tubes containing the gas, and immediately place the palm of one hand snugly against the mouth of the tube, which I shake vigorously for a minute. At the end of this time I can demonstrate the solubility of the gas. The outstretched hand can easily support the partially evacuated test tube.

Third, I attach two clamps to the ring stand to support two test tubes containing the gas, one inverted and the other mouth up, the mouths as close together as possible. After one minute I bring a lighted splint to both mouths. The gas in the upright test tube burns; that in the inverted one is not flammable.

Hydrogen sulfide is obviously denser than air and is also combustible.

Fourth, I displace water in a large test tube to about one inch in height, while in another I displace all the water by the gas. Then I allow the water in the first test tube to pour out quickly, while the test tube is kept inverted. In this test tube is a mixture of the gas and air in the proportion of about one to seven. When a lighted splint is brought to the test tube that is completely filled with gas, the gas burns slowly in this limited supply of air, with a copious deposit of sulfur according to this equation:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

When a lighted splint is brought to the mouth of the second tube a flame shoots down the tube. Almost no sulfur is deposited. When the odors from the two experiments are compared, the former is found to be almost odorless while the second has the sharp, pungent odor of sulfur dioxide. The equation for the latter reaction is as follows:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

MILTON G. WOLF

JAMES MADISON HIGH SCHOOL
BROOKLYN, NEW YORK

To the Editor:

I have just finished reading "Let's Use Problems to Teach Chemistry," by James G. Traynham, in the February issue. I find myself in complete agreement with the author. The reasoning approach should be used as far as possible even in high-school chemistry. Problems done by simple proportions mean nothing to the understanding of the chemical principles that are involved.

High-school texts and laboratory manuals do fail here. It sometimes seems that the aim of the text is to make it so simple for the student as to avoid explaining the reasoning behind a principle. I have found at least one laboratory manual that is now stressing the reasoning approach in doing some of the quantitative experiments.

I have found that high-school pupils in the college preparatory group find the reasoning approach more difficult and confusing at first, but after a few months the method of reasoning is proof against error in calculations. They seem to understand that the answer is not the most important thing when learning the principles of the subject.

In general, it seems better to teach the student to reason out the problem and to use units for everything in the problem, even in high school. I agree with Mr. Traynham completely.

BROTHER BONAVENTURE, C.F.X.

ST. XAVIER HIGH SCHOOL
LOUISVILLE, KENTUCKY

Recent Books

CHEMISTRY OF CARBON COMPOUNDS. VOLUME IIA: ALICYCLIC COMPOUNDS

Edited by *E. H. Rodd.* Elsevier Publishing Co., Houston, Texas, 1953. xxiv + 487 pp. 16 × 23.5 cm. Subscription price, $11.25; single volume price, $12.50.

For an appraisal of the plan of the Elsevier series on the "Chemistry of Carbon Compounds" and criticisms of Volumes IA and IB, the reader's attention is called to the reviews of T. L. Jacobs, THIS JOURNAL, **30**, 100 (1953) and W. A. Bonner, THIS JOURNAL, **30**, 158 (1953).

All but 80 pages of Volume IIA was written by R. A. Raphael on alicyclic compounds of three to many members, spiranes, condensed systems, and bridged ring systems; R. F. Hunter contributed a chapter on carotenoids which contains 24 references to his own work; and R. G. R. Bacon wrote the chapter on olefinic polymers, both open-chain and ring. This last chapter, largely on rubber chemistry, was arbitrarily put in this volume.

The chapter on carotenoids is perhaps the best, as might be expected of an author who is a current worker in a restricted field. He has an excellent critical review of the work of Karrer, Kuhn, and Zechmeister.

About one-fourth of the book is devoted to cyclohexane derivatives, the largest group of alicyclic compounds.

Whereas Whitmore's "Organic Chemistry" competes favorably with Volume IA (see T. L. Jacobs' review) in the series, there is no intermediate secondary source on alicyclic compounds as good as the present volume.

There is a remarkable number of references to work after 1950 in the present volume. The index of about 40 pages has more than 4000 entries.

I have no adverse criticisms of Volume IIA beyond the general ones of Jacobs and Bonner, with which I agree.

An additional sheet of addenda and corrigenda to Volume I is included; these are all of a minor nature or obvious.

LEALLYN B. CLAPP

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

GENERAL CHEMISTRY

***Linus Pauling,* Professor of Chemistry, California Institute of Technology. Second edition. W. H. Freeman and Co., San Francisco, 1953. xii + 710 pp. 193 figs. 2 plates. 16 × 24.5 cm. $6.**

THE second edition of Pauling's "General Chemistry" has three new chapters, and many others have been completely rewritten to make it, as the author states, "especially suited to use by first-year college students who plan to major in chemistry and by other well prepared students with a special interest in the subject." Admittedly this is not a text for the student with a mediocre background in high-school mathematics and physical science, but instructors who feel they cannot use it will wish that they could.

Most of the drawings and diagrams of the first edition have been retained and many equally excellent new drawings have been added. Mr. Hayward, the illustrator, has a remarkable ability to convey solidity or a three-dimensional effect, as the readers of the first edition already know. The paper is better, the print seems easier to read, and the setup has been improved, *e. g.*, problems are separated by a space.

In spite of some deletions and condensations of material from the first edition, the expansions and additions have added 120 more pages. Dr. Pauling suggests that there is "perhaps 10%" more material than can be covered in a one-year course, so that the instructor has some flexibility in presentation.

Some of the improvements and additions are the many new, excellent drawings; more *evidence* for some of the dogmatic statements many of us use, particularly for the structures of atoms, crystals, and molecules: *cf.* new Chapter 3 on Electron and the Nucleus and new Chapter 8 on Quantum Theory and Molecular Structure; the "common-sense" approach to the solution of gas-law problems; dimensions and units appear in fine print on page 7, but are not fully utilized; an energy level diagram modified from Pauling's "Nature of the Chemical Bond" which this reviewer has found particularly helpful for several years; many clarifications, *e. g.*, the first edition used the term "optical activity" but said nothing about it, while the new edition uses the term "right and left-handed molecules" and proceeds to clear up the subject; and Biochemistry, new Chapter 29, with, among others, drawings of the helical structure of some proteins. Some philosophy of science is woven unobtrusively through the text; *e. g.*, reality and explanation; the sequence of theory, prediction, and discovery; do electrons exist? what do electrons look like? and the possibility of transfer of the usefulness of the scientific method to fields other than science. The interdependence of chemistry, physics, and mathematics is well demonstrated.

Chapter 1 omits "what a chemist does" and "why study chemistry?" All summary lists of concepts are omitted from the ends of chapters. For the students who used them this seems a lamentable deletion but perhaps this exemplifies the paradox that an aid intended for the poorer students is used largely by the better. The index, although large, is not complete enough. One cannot ask a book questions, so the best possible index should be available. Some omitted terms are: concentration, molar, formal, normal, molal, weight molarity, standard conditions, system, calorie, saturated solution, equivalent, equivalent weight, atomic mass unit, accuracy, precision, dimension, units, etc.

This second edition is a fine example of the fact that the excellent (first edition) is still improvable. Its use will be a delight to the well prepared chemistry or science major and also to the instructor.

H. C. BENEDICT

CHICO STATE COLLEGE
CHICO, CALIFORNIA

STRUCTURE AND MECHANISM IN ORGANIC CHEMISTRY

***C. K. Ingold,* Professor of Chemistry, University College, University of London. Cornell University Press, Ithaca, New York, 1953. vii + 828 pp. 159 tables. 37 figs. 16 × 24 cm. $9.75.**

THIS book is the culmination of thirty years of research and thought on the subject of organic chemical reaction mechanism by Professor Ingold, who is generally recognized as the most eminent figure in this field today. This volume lives up to the

reputation of its author in all respects. It is detailed and exhaustive in its treatment of the main subjects; the large number of tables indicates that it is well documented; and in addition the author has usually included a very interesting historical perspective at the beginning of each major section. It is an advanced treatise and one which scarcely would be appreciated by any but the advanced student and teacher in the field.

Nowhere else will there be found a review of Electrophilic Aromatic Substitution, Nucleophilic Aliphatic Substitution, or Olefin-forming Eliminations which will compare to the treatment here. If one includes related material, the subject of aromatic substitution occupies 190 pages, or almost one-fourth of the 816 pages of text. This is indicative of the extent and detail of the treatment. Illustrative material in these sections is drawn from many sources and Professor Ingold has shown a tremendous breadth of knowledge concerning the work in the field of organic reaction mechanism. As is only natural, however, he has relied heavily upon his own and closely related investigations for most of the material, as indicated by the fact that 105 of the 231 references in the chapter on Nucleophilic Aliphatic Substitution are to Ingold and Hughes, separately or jointly. There is thus no question concerning the authority with which the author writes and there is also no question but that the viewpoint (and also the terminology) of the English school is held throughout. In several instances other viewpoints have been ignored by omission or dismissed in a summary fashion.

As stated by the author in the preface, "the wide scope of the subject has necessitated the imposition of limitations.... Thus a very appreciable fraction of the field indicated by the title remains uncovered." This is especially true of the treatment of "structure" which is limited to the introductory chapter on Valency and Molecular Structure, a section of the chapter on The Aromatic Nucleus, and those aspects of stereochemistry which naturally come up in connection with Nucleophilic Aliphatic Substitution, Olefin-forming Eliminations, Saturated Rearrangements, and Additions and Their Retrogression. The selection of material necessitated the omission of many pertinent subjects; the following is a list of a few that the reviewer did not find included: free radical reactions in general, polymerization, catalytic reduction, the mechanism of most oxidation processes, the problem of conformation or constellation, the subject of bridged ions, Grignard reactions, rearrangements of the Baeyer, Villiger, and Criegee types, and hindered rotation in the biphenyl series. In addition the subject of cyclic mechanisms is only mentioned; for instance, the Tschugaev reaction was not taken up in the section on olefin-forming eliminations. An inadequate index has measurably lessened the value of this volume as a reference text.

These shortcomings of omission cannot detract from the excellence of the volume as a definitive treatise of Ingold's contribution in the field of organic chemical mechanism and there is no question but that it will have an honored place in the permanent chemical literature.

HARRY S. MOSHER

Stanford University
Stanford, California

● ORGANIC PROTECTIVE COATINGS

Edited by *William von Fischer,* Head, Department of Chemistry and Chemical Engineering, and *Edward G. Bobalek,* Associate Professor of Chemistry, Case Institute of Technology. Reinhold Publishing Corp., New York, 1953. viii + 387 pp. Many figs. and tables. 16 × 23.5 cm. $7.50.

Case Institute of Technology has built up a reputation in the field of paint and varnish technology which had to be broadened in scope as various organic protective coatings entered the field of surface protection. In 1948 Dr. von Fischer edited a series of lectures that had been given at Case by a number of experts. This was published as "Paint and Varnish Technology." Now the panel of experts has broadened its field of discussion and "Organic Protective Coatings" is the result.

A variety of materials are discussed in the sixteen chapters of this book. Synthetics dominate the field, with vinyl resins occupying the most attention. Others are aminoplast resins and the silicones. Pigments are discussed in several chapters, anticorrosive pigments, reflectance properties, luminescent coatings, new pigments in modern color design, and pigment dispersion problems in formulation. The formulation of emulsion and latex paints is discussed on the basis of emulsion systems.

Although this book does not cover all recent advances, or discuss all subjects exhaustively, it helps keep the technical man abreast of developments in the broadening field of protective coatings. Taken with the earlier book, the two volumes are excellent reference texts in this field.

KENNETH A. KOBE

University of Texas
Austin, Texas

● RELATIVITY AND REALITY

E. G. Barter. The Philosophical Library, Inc., New York, 1953. xi + 131 pp. 13.5 × 21.5 cm. $4.75.

The author has undertaken in this slim little volume to clarify certain interpretations and applications of relativity to make them more acceptable to the classical physicists. In this work his objective appears to be carefully to point out where some writers have failed to distinguish between the well established evidence and that which represents a degree of uncertainty and/or of individual opinion.

Absolute space at rest, the constancy of the velocity of light, the reciprocity of distortions, reality, and similar concepts subject to duo-interpretation are re-examined as metaphysical and as natural science concepts with an attempt to bring them to a common focal point.

Those scholars learned in both philosophy and physics will find the book interesting and provocative. The general reader will find it beyond his ken.

SISTER MARY MARTINETTE, B.V.M.

Mundelein College for Women
Chicago, Illinois

● DISLOCATIONS IN CRYSTALS

W. T. Read, Jr., Bell Telephone Laboratories, Murray Hill, New Jersey. McGraw-Hill Book Co., Inc., New York, 1953. xvii + 228 pp. 77 figs. 16 × 23.5 cm. $5.

Scientific understanding of the properties of metals, alloys, and other solids has been greatly advanced by the determination, using X-ray diffraction methods, of the arrangements of atoms in the hypothetical, perfectly regular, structures which the actual structures approximate. It has long been evident, however, that certain properties, especially those (*e. g.*, tensile strength and hardness) which involve changes in the relative locations of the atoms, are "structure-sensitive." These properties often depend more on deviations from the perfect structure than on the nature of the structure itself.

Such structural deviations or imperfections are of various kinds. One type consists of a foreign atom, together with the disturbed region immediately surrounding it. "Dislocations" constitute another important class. A dislocation is an imperfection which can be considered as being produced by slipping of a portion of the regular structure relative to the rest. It consists of a distorted region in the neighborhood of a line in the structure.

The book under review deals with the nature, description, classification, geometry, and physics of dislocations and their

motions through the crystal. The emphasis throughout is on metals, but the same principles obviously apply to other solids. The only applications considered in any detail are those to crystal growth and to grain boundaries in metals. The author realizes, of course, that dislocations are of paramount importance in the field of mechanical properties—strength, plastic formation, work hardening, etc.—yet he avoids the theoretical treatment of these subjects. "Instead of reviewing current speculations (or adding others), [he has] tried to give the student and prospective researcher a sound foundation that will enable him to attack these problems successfully and eventually bring them from the area of speculation into the area of applied science."

This book is clearly written and admirably illustrated by many line drawings. Many pertinent exercises are included. Advanced students interested in the physics of metals should find it very useful, either for individual study or as a textbook for a course in dislocation theory. The reader is assumed to be familiar with elementary calculus, but not with crystallography, beyond the most fundamental ideas.

The publisher's job, like the author's, has been well done.

MAURICE L. HUGGINS

EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK

● SOILS AND FERTILIZERS

Firman E. Bear, **Professor of Agricultural Chemistry, Rutgers University; Research Specialist in Soils, New Jersey Agricultural Experiment Station. Fourth edition. John Wiley & Sons, Inc., New York, 1953. xiii + 420 pp. 101 figs. 157 tables. 15.5 × 23.5 cm. $6.**

THIS is a completely revised textbook designed for use in beginning courses in soils for students in general agriculture. It particularly stresses the relationship existing between soils and crop production and the conservation of one of our major natural resources, the soil. For the serious student majoring in soils it is lacking in the advanced phases of scientific and technical details. The subject matter is well documented with tables and graphs of data plus many illustrations.

E. A. FIEGER

LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA

● STANDARD METHODS OF CLINICAL CHEMISTRY. VOLUME I

The American Association of Clinical Chemists. Editor-in-Chief, *Miriam Reiner,* Director, Chemistry Laboratory, Gallinger Municipal Hospital, Washington, D. C. Academic Press, Inc., New York, 1953. xii + 142 pp. Illustrated. 16 × 23.5 cm. $4.50.

THE purpose of this volume is to check certain methods in common use in clinical laboratories and to explain the scientific basis of each method. It is written for "countless laboratory workers, chemists and technicians." It is to be comparable to the methods of analysis put out by the Association of Official Agricultural Chemists. Each method has been used and checked by one or more of the member chemists. Volume I covers routine examinations: amylase, bilirubin, calcium, CO_2 content, chlorides, free and total cholesterol, creatinine, glucose, lipase, phosphatases and inorganic phosphates, total proteins, albumin and globulin, prothrombin, sodium and potassium flame photometry, thymol turbidity, urea nitrogen, uric acid. Author and subject indexes are complete.

The Editorial Committee decided on a collection of small volumes because "this insures great flexibility . . . it permits the issuance of handy volumes for use at the laboratory bench and the current presentation of new and timely methods and modifications." Sometimes one procedure is given, rarely three. Any worker in the clinical field realizes there is need for a guide. Unique tests with unique equipment are often offered to the market which could well be rated in a book of standard procedures.

Small volumes such as this one, only listing the methods found in standard texts that are approved by the Committee, and giving in detail new modifications or methods not available in such standard texts when they have been approved, might be bound in cheaper paper covers.

A discussion of the advantages and disadvantages of such methods would be a great help to clinical technicians. A reader might also be interested in knowing why the particular modifications of existing standard methods have been adopted. It is a stupendous undertaking to establish standard procedures for all workers.

VIOLA SOMMERMEYER

SAN DIEGO, CALIFORNIA

● COMPREHENSIVE INORGANIC CHEMISTRY. VOLUME II: COPPER, SILVER, AND GOLD

Edited by *M. Cannon Sneed,* Professor of Chemistry, *J. Lewis Maynard,* Professor of Chemistry, and *Robert G. Brasted,* Associate Professor of Chemistry, University of Minnesota. D. Van Nostrand Co., Inc., New York, 1954. x + 248 pp. 16 × 23.5 cm. $5.

THIS book, by James W. Laist, covers the descriptive chemistry and the extractive metallurgy of the "coinage metals" with near equal space devoted to each topic. The fact that much of the chemistry of these elements is concerned with mining operations explains this division.

An introduction gives tabulations of the physical, chemical, and nuclear properties of this triad and briefly characterizes their chemistry in terms of electronic structures. Each element is then individually treated on the basis of its history, natural occurrence, recovery processes from ores, commercial alloys, and the chemical properties of the metal and its alloys. The writing is clear and the book is adequately filled with references and necessary illustrations.

The utility of this nonthermodynamic treatment is as a reference text in undergraduate inorganic courses. The advanced research worker will probably consult the better known systematic treatises. However, the captivating style of the book will draw the lay "popular science writer" to it as a source of information.

EDWARD D. GOLDBERG

SCRIPPS INSTITUTION OF OCEANOGRAPHY
LA JOLLA, CALIFORNIA

● BIOCHEMICAL PREPARATIONS. VOLUME 3

Esmond E. Snell, **Editor-in-Chief. John Wiley & Sons, Inc., New York, 1953. viii + 128 pp. 15.5 × 23.5 cm. $3.50.**

THE third volume of "Biochemical Preparations" advances substantially the enviable reputation established by the preceding volumes of this significant work. The book makes an immediate appeal to the teacher and research worker by setting forth, for each preparation, synonymous names, formula, and molecular weight; clearly written and easily followed equations presenting the principle of the method; names and addresses of contributors; concise and pertinent notes; and essential references to the literature.

The consideration which is given to the selection of starting materials, particularly in this field of biochemistry, is in itself an invaluable feature. The procedures, including sizes of vessels and quantities of materials, are clear and easily followed. The

breakdown into well indicated steps, followed by sections on properties and purity, provides for the experimenter exactly what he desires and needs. The use of the present tense, passive voice in giving directions is pleasing as well as adequate.

The book carries a complete subject index and a list of 64 compounds of biochemical interest which have appeared in "Organic Syntheses" through Volume 32.

Beginning in many cases with natural sources of materials, the book describes 26 preparations, including crystalline muscle phosphorylase, ribonuclease, diphosphopyridine nucleotide (DPN), triphosphopyridine nucleotide (TPN), pyridoxamine phosphate, pyridoxal phosphate, protoporphyrin dimethyl ester, *d*-isocitric acid, *dl*-isocitric acid lactone, dihydroxyfumaric acid, oxalacetic acid, L(+) and D(−)lactic acids, sodium α-ketoisocaproate, D-glucose-6-phosphoric acid, D-galacturonic acid, β-2,5-dihydroxyphenyl-DL-alanine, L-isoleucine, D-isoleucine, L-alloisoleucine, D-alloisoleucine, L- and DL-ornithine monohydrochlorides, L- and DL-citrulline (from ornithine), L-citrulline (from L-arginine), L-kynurenine, L- and D-penicillamine hydrochlorides, elaidic acid, 2,4-dinitrofluorobenzene.

EARL M. BILGER

University of Hawaii
Honolulu, Hawaii

● HISTOCHEMISTRY: THEORETICAL AND APPLIED

A. G. Everson Pearse, Lecturer in Histochemistry, Postgraduate Medical School, University of London. Little, Brown and Co., Boston, 1953. viii + 503 pages. 109 figs. 4 plates. 15.5 × 23.5 cm. $12.

This book is presumably addressed to two main groups of readers: those performing routine clinical histochemical determinations and those research workers in other fields desiring to apply histochemical techniques to specific problems. The reviewer is qualified to speak to and for only the second of these groups and will consider the book from their standpoint.

The author calls in his preface for a wider application of histochemistry, and adds that such application depends on greater awareness of the possibilities of available techniques. A main purpose of the book, then, is to compile for the nonspecialist information on the potentialities, limitations, and comparative advantages of individual methods. It would appear that this objective has been in general very well achieved.

Methods for the detection of individual compounds or types of compounds are discussed in the body of the book, while the detailed directions for the recommended methods are grouped in an appendix. This organization seems a desirable one, at least from the standpoint of the occasional user, in that a comparative discussion of the different methods for a given constituent need not be broken up by recipes and procedural directions. Each description of a method in the appendix includes a brief statement of the results and degree of specificity to be expected, so that the more detailed treatment in the main text need not necessarily be consulted.

Some portions of the book seem aimed only at the needs of routine clinical technicians, rather than at those of the larger audience of workers in related fields whom the author hopes to reach. The treatment of fixation appears rather inadequate, and seems to be limited mainly by the feeling that, since the clinical worker may generally receive samples already fixed in formalin, "it is better to become reconciled to the evils" of such fixation than to arrange for other processing. Other methods are therefore not extensively considered. Certainly the nonclinical research worker will have his procedures under more personal control, and he may be as greatly in need of advice on fixation as on histochemical determinations. Similarly, methods for metals are limited to those "which may be required in routine diagnostic histochemistry," and plant histochemistry is entirely ignored except for the historical section.

The frequent use of abbreviations for reagents or procedures may disconcert the reader seeking information on a particular determination, since he may need to skim back twenty or more pages to find their meanings. Reference to the index is frequently, but not always, helpful. In the same connection, methods in the appendix are preceded by cryptic symbols suggesting the preferred prior processing of the sample. The infrequent user of the book will devote too much time to finding the inconspicuous table which allows him to decode these recommendations.

Despite these minor inconveniences, the biologist or biochemist desiring to explore the applicability of histochemical methods to a specific problem may well turn first to Pearse's book. The treatment seems comprehensive, a conscientious effort is made to present the chemistry involved whenever possible, and the limitations and deficiencies of each procedure are critically discussed. Although frankly seeking to proselytize nonhistochemists, the author avoids exaggerated claims for his discipline. Accordingly, few among his converts should become disillusioned apostates.

D. E. ATKINSON

University of California
Los Angeles, California

● FOAMS: THEORY AND INDUSTRIAL APPLICATIONS

J. J. Bikerman, in collaboration with R. B. Booth, American Cyanimid Co., J. M. Perri, National Foam Co., and C. C. Currie, Dow-Corning Corp. Reinhold Publishing Corp., New York, 1953. ii + 347 pp. 62 figs. 16 × 23.5 cm. $10.

"This volume was written for scientists who intend to profit by foam or are plagued by it, or last but not least, are interested in foam just because foam is so interesting." The authors have made foam both interesting and practical.

Mr. Bikerman has prepared the first eleven chapters dealing with the fundamental properties of foam as a colloid system. These properties are given basic treatment with ample reference to the prior literature.

Mr. Perri describes the fire-fighting foams used so successfully by the Navy during the war, and now used by industry.

Mr. Booth discusses froth flotation, the basis of an ever increasing use of foam for the benefication of low grade ores or separation of chemical compounds.

Mr. Currie surveys the literature on chemical antifoaming agents for the benefit of those plagued by foams.

This book is of interest to the colloid chemist for its basic treatment of foams and to the technologist who must use or destroy foam.

KENNETH A. KOBE

University of Texas
Austin, Texas

● BIOCHEMISTRY AND PHYSIOLOGY OF NUTRITION. 2 VOLUMES

Edited by Geoffrey H. Bourne, London Hospital Medical College, England, and George W. Kidder, Amherst College. Academic Press, Inc., New York, 1953. Vol. I, xiii + 569 pp. $13. Vol. II, xi + 641 pp. $15. Illustrated. 15.5 × 23.5 cm.

This authoritative work by 14 British and 14 American writers is a timely publication. It is practically a treatise on biochemistry, since it covers so much of the dynamic aspects of the subject. The first two chapters deal with historical aspects of nutrition, especially the history of vitamin discoveries. Then follows a group of chapters on metabolism of water, electrolytes, carbohydrates, amino acids, protein synthesis, and lipids. The biochemistry of the fat-soluble vitamins and of the vitamin B complex are each treated in a single chapter.

A chapter by T. H. Jukes on vitamins and hematopoiesis discusses the complex behavior of folic acid and related compounds,

and of vitamin B_{12}. The occurrence in saliva of something related to the intrinsic factor is not mentioned. A long chapter by B. B. Lloyd and H. M. Sinclair deals with vitamin C and includes the various theories as well as the proved facts of its functioning. This concludes Volume I.

In Volume II there are two chapters by G. H. Bourne on histological aspects of vitamin physiology and a chapter by G. W. Kidder on nutrition of invertebrate animals. Of the twelve chapters in this volume, the one by G. D. Novelli and M. Soodak on coenzymes is particularly useful because it gathers together a wealth of detailed information on a complex subject. There are three chapters on the metabolism of inorganic elements. The final chapter, by G. A. Goldsmith, summarizes the applications of nutritional discoveries to human nutrition.

Discoveries in the science of nutrition occur so rapidly that older books on the subject tend to be out of date. A new and well planned treatise of this sort is therefore very welcome to all who are interested in this subject that is fundamental for human welfare.

PHILIP H. MITCHELL

Brown University
Providence, Rhode Island

● MARGINAL PUNCHED CARDS IN COLLEGE AND RESEARCH LIBRARIES

Howard F. McGaw. The Scarecrow Press, Washington, 1952. 218 pp. Illustrated. 13.5 × 6 cm. $4.50.

This book describes and illustrates edge-notched punched cards and equipment supplied by each of various manufacturers as well as basic sorting techniques and a variety of coding methods.

About two-thirds of the book is devoted to detailed description and illustration of library applications. The circulation, acquisitions, serials, reference, bindery, and other departments are covered. In an appendix are listed the libraries using edge-notched punched cards.

The right-hand margins of the printed pages are not justified. The illustrations are poor. An inconvenience is that footnotes are listed at the end of each chapter along with literature citations. A bibliography of 87 references is given at the end of the book.

The author's objectives are: "First, to provide a guide book to the librarian just beginning his exploration of the uses of marginal punched cards and, second, to call to the attention of those who have been working with such cards, some of the techniques and applications about which they possibly have not heard." These objectives are fulfilled.

ROBERT S. CASEY

W. A. Sheaffer Pen Company
Fort Madison, Iowa

● CHEMICAL METHODS IN INDUSTRIAL HYGIENE

Frederick H. Goldman, Bureau of Public Health Engineering, Government of the District of Columbia, and *Morris B. Jacobs,* Department of Air Pollution Control, City of New York. Interscience Publishers, Inc., New York, 1953. x + 274 pp. 24 figs. 7 tables. 13 × 18.5 cm. $3.75.

This is a manual, by recognized authorities, designed to serve the analyst in the field of industrial hygiene in his choice of method. The methods presented are for the ordinary chemical laboratory. Field tests and the use of specialized apparatus are not covered.

The scope of the manual is indicated by the general topics covered: Sampling, Preparation and Standardization of Reagents, Particle Size Determinations, Free Silica, Inorganic Compounds and Gases, Metals, General Methods for Volatile Solvents, Organic Solvents, Miscellaneous Gases, Vapors, and Mists. There are about one hundred specific tests in addition to much material on general procedures. The emphasis is on environmental and particularly airborne contamination.

Table 5 in the Appendix is the Threshold Limit Values as adopted by the American Conference of Industrial Hygienists, though for the year 1952. Table 7 is a useful outline, listing for about a hundred materials collecting media, sampling apparatus, sampling rate, analytical method, and page reference. The bibliography lists 114 references to the literature which are included in the general subject index for the manual.

This is an Interscience Manual, one of four in a proposed series of laboratory manuals, and is an excellent example of a useful presentation by competent authors.

PHILIP GILL

Office of Civil Defense
Hollywood, California

● ANTIBIOTICS

F. A. Robinson. Pitman Publishing Corp., New York, 1953. viii + 132 pp. 14 tables. 14 × 22 cm. $3.

A qualified British investigator has here reduced a large volume of information on antibiotics to a short, authoritative, and highly readable and interesting text. Following as it does the publication by others of detailed reviews, monographs, and handbooks devoted to antibiotic substances, Robinson's book presents an abbreviated but satisfying picture of the subject as a whole and one that should be especially valuable to students of biochemistry and bacteriology.

Major emphasis is placed on the chemistry and biochemistry of the best known antibiotics (penicillin, streptomycin, chloramphenicol, aureomycin, terramycin). Bacteriological applications are restricted largely to summation of antimicrobial spectra, and the discussions include short sections on pharmacology and clinical applications. Very brief notice is given also to additional antibiotics synthesized by actinomycetes and by bacteria; for example, actinomycin, streptothricin, neomycin, tyrothricin and its components, subtilin, and bacitracin. The monograph is concluded with a classified and selected bibliography of some 40 entries and has a subject index.

The book is timely. To a degree it serves to supplement certain information made available in earlier reviews and already antiquated by the current pace of antibiotic research. But more important is its function as a survey aid, a means by which the reader can step aside from the mounting accumulation of technical papers to appraise the developments that have brought the antibiotic picture to its present level. It is a type of publication that could serve as well in other expanding fields.

WILLIAM D. ROSENFELD

California Research Corporation
La Habra, California

● TABLES OF INTEGRAL TRANSFORMS. VOLUME I

Edited by *A. Erdélyi,* with *W. Magnus, F. Oberhettinger,* and *F. G. Tricomi,* Research Associates, staff of the Bateman Manuscript Project, California Institute of Technology. McGraw-Hill Book Co., Inc., New York, 1954. xx + 391 pp. 16 × 24 cm. $7.50.

This volume is the first of two intended as companions and sequels to the authors' "Higher Transcendental Functions," and is based in part on notes left by the late Harry Bateman. Included are Fourier, Laplace, and Mellin transforms and their inversions.

Out of the Editor's Basket

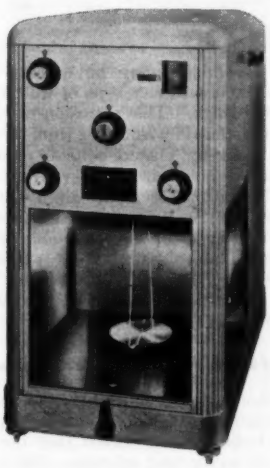
Right-A-Weigh Balance

Wm. Ainsworth & Sons, Inc., 2151 Lawrence St., Denver, Colorado, has just announced that it is now in production on its new Right-A-Weigh one-pan, constant sensitivity balance.

The Right-A-Weigh balance has a capacity of 200 g. and a sensitivity of $^1/_{10}$ mg. It is said to be much faster and easier to use than a conventional analytical balance.

Handling of separate weights is eliminated. All the necessary weights are built into the balance and are operated by knobs on the front of the case. The knobs also operate counters which show the total of the weights employed. Values from $^1/_{10}$ mg. to 100 mg. are read from a projected scale to the right of the counters.

The weights and the pan are suspended from the same end of the beam. In weighing, weights equal to the load added to the pan are removed from above the pan. This substitution method of weighing is most accurate, and with a constant load on the beam, the balance has the same sensitivity regardless of the load on the pan.



Many convenience features make the balance easy to use, and a high-grade optical system makes it easy to read the projected scale. As a result, even inexperienced personnel can weigh quickly and accurately on the Right-A-Weigh balance.

Laboratory supply houses now have the Ainsworth Right-A-Weigh balance and complete data are available from them or from the manufacturer.

Magnetic Stirrer

Scientific Glass Apparatus Co., Inc., announces the development of a new stirrer, known as the "Lew" Magnetic Stirrer, for vacuum, pressure, or atmospheric work. Liquids up to a consistency of glycerin can be agitated.

According to the manufacturer, the design is unique in that the powerful magnetic field is located above the vessel proper, leaving the underside entirely free for the application of heat or cold. This prevents the possibility of glass breakage caused by friction between the stirring magnet and the "Pyrex" glass flask.

Two models are available; the Vacuum and/or Pressure Model and the Atmospheric Model.

For complete information, write directly to the Scientific Glass Apparatus Co., Inc., Bloomfield, New Jersey.

Double-Purpose Power Supply

Suitable for a wide variety of laboratory power-supply applications, the new Spinco Duostat includes, in a single unit, facilities for both constant-current operation and constant-voltage operation.

Energized from a standard 115-v 50/60 cps power outlet, the Duostat is capable of providing currents ranging from 5 to 50 milliamperes, automatically regulated to ±2 per cent at voltages ranging from 100 to 500 volts. In its constant-voltage mode of operation, the unit is self-regulated to ±1 per cent from 160 to 500 volts, and over a load-current range of 0 to 50 ma. Output is relatively unaffected by line-voltage changes between 105 and 125 volts.

Additional data may be had by writing

GLISTENING WHITE CHEMICAL PORCELAIN
Invites LABORATORY CLEANLINESS
VACUUM FILTERS
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MIXING VESSELS
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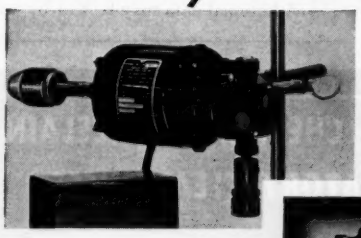
But even more important than the appearance of cleanliness is the purity and safety of "U. S." white chemical porcelain itself. Completely iron-free, chemically inert, dense, impervious, chemical porcelain is the ideal material for handling fine chemicals — both in laboratory and production.
2350
THE U. S. STONEWARE COMPANY
CERAMICS DIVISION
AKRON 9, OHIO

a New Bridge to Laboratory EFFICIENCY

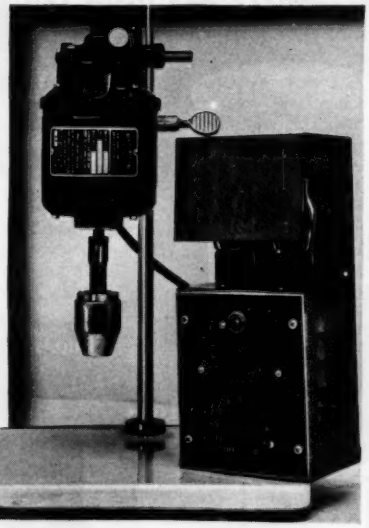
ELECTRONIC CONTROLLED

LABORATORY STIRRER

with Thyratron Tube Control



Direct and gear drive in one fully enclosed ball bearing motor. Variable Speed at full torque. 1/50 H.P. motor. Can be run in either direction.



The speed on direct drive ranges from 400 rpm to 5000 rpm in stepless control. The speed of gear-driven shaft is 1/18 the direct or armature speed.

Starting torque on armature is 32 in ounces. May also be used to drive constant speed devices. Stirrer can be attached to ordinary laboratory support stand.

STIRRER

Motor is driven by a phase shift Thyratron Tube controlled rectifier, which converts the alternating current of the mains to direct current. Field and armature of motor are fed separately by two—2050 gas rectifier tubes. **Price $89.50**

For Data on this
Newest of the new Laboratory Stirrers
Write Dept. ES—C

ACE GLASS INCORPORATED
VINELAND NEW JERSEY

Specialized Instruments Corp., 670 O'Neill Ave., Belmont, California.

Sterilizers in the Wall

For the modern laboratory, often crowded for space, Precision Scientific Co. has developed a Flush-Mounting Assembly for "Precision-Freas" ovens, sterilizers, and incubators. The polished, stainless steel panel units permit bulky cabinets to be recessed in tile, brick, concrete, or plaster walls.

The Flush-Mounting Assemblies are stock units. A dial thermometer with large, readable numerals is recessed in the top of the panel—a striking improvement over conventional, difficult-to-read glass thermometers.

The assemblies may be quickly and easily attached to any type of wall up to 11½ in. thick. The corrosion-resistant panel is fastened by clamping from behind, rather than by visible bolts or screws; the wall is not marred. Seven sizes of Flush-Mounting Assemblies are available, designed to fit both gravity and mechanical convection types of sterilizers and ovens. Complete information, with cut-away drawings, will be sent on request by Precision Scientific Co., 3737 W. Cortland St., Chicago 47, Illinois.

Preparation of Hydrogen Selenide

K. R. V. Rao and A. Viswanathan of the Minerva Tutorial College, Madras, South India, have observed that the hydrides of sulfur and selenium, which are members of the same chemical family, can be produced by many reactions that are similar. A simple method of generating selenium hydride is to heat 0.1 g. of red selenium powder with 5 g. of paraffin wax in a test tube fitted with a delivery tube. The gas is steadily evolved in sufficient quantity to carry out experiments similar to those under hydrogen sulfide. Various colored metallic selenides can be precipitated from metallic salt solutions, and solutions of potassium permanganate, and the halogens, etc., can be reduced.

The gas ceases to evolve when the burner is removed, and the residue in the tube can be used repeatedly to produce the

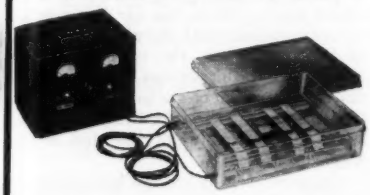
gas. As the gas possesses a disagreeable and persistent odor, its preparation should be conducted in a good draft of air or in a hood.

New Labline Electrograf

Labline's new Electrograf, developed by Dr. E. Philip Halpern, formerly Bio-Chemist, Albert Einstein Medical Center, opens a new, simple, and important avenue to the analyst for the quantitative and qualitative study of materials exhibiting electro-migrating characteristics.

This new Electrograf for running paper electrophoresis determinations has been designed to offer the technician a low-cost, easily operated unit with great flexibility. The migrating chamber is molded, one-piece transparent plastic, accommodating twenty $\frac{1}{2}$-inch wide filter strips or twelve 1-inch wide filter strips, with voltage control from 0 to 450 volts, and current control from 0 to 50 milliamperes. The power supply has sufficient capacity and is equipped with necessary plug-ins to operate four migrating chambers simultaneously.

By far the majority of applications of paper electrophoresis have been made in the fields of biochemistry or clinical chemistry; however, the magnitude of applications has now spread to the organic, inorganic, and physical chemistry fields.



To obtain uniform migration patterns, an electrophoresis apparatus should be operated at constant temperature and humidity, with constant voltage and current input to the electrodes. Migrating materials must be protected from unfavorable pH changes due to accumulation of electrode products. Syphoning through paper strips must be prevented.

The Labline Electrograf meets these conditions of performance. The migrating chamber will fit into any refrigerator to maintain constant temperatures. Constant humidity is created with a snug fitting cover. Constant voltage and current is produced with the new Labline specially designed power supply. Protection of migrating materials is done with separate troughs for electrodes and buffer. Cotton wicks connect electrode troughs with buffer and automatic liquid leveler prevents syphoning of buffer through paper strips.

Detailed information about the Electrograf may be obtained from the manufacturer, Labline, Inc., 217 N. Desplaines St., Chicago 6, Illinois.

Thermometric Bridge

The Sargent Thermometric Bridge is a thermistor-actuated sensing bridge with output controls permitting the direct use of galvanometers or potentiometric recorders. Useful for measuring and recording differential temperatures over the range 0 to 100°C., this unit has been used for testing performance characteristics of constant-temperature baths and thermoregulators. When it is used with galvanometers of moderate sensitivity or recorders having full scale equivalents of a few millivolts, a measuring precision of plus or minus several thousandths of a degree centigrade is practicable over the range given above.

To secure complete information, refer to item S-81600 and address the Advertising Dept., E. H. Sargent & Co., 4657 West Foster Ave., Chicago 30, Illinois.

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Quartz Immersion Heater

Fisher Scientific Co. announces its new Glo-Quartz immersion heater. It is a wand of fused quartz, less than one-half inch in diameter, that encases a 400-watt heating coil, and it can be held in the bare hand while seven of its twelve inches glow red-hot. Placed in a reaction flask it gives instant, concentrated heat exactly where heat is wanted.

Because of the resistance of quartz to thermal shock, the Fisher Glo-Quartz Heater does not crack, break, or short-circuit under this treatment. It can be used glowing-hot directly in an acid bath.

The heater is also a good source of infrared. The nickel-chrome heater, operating at 1700°F., radiates strongly in the far infrared, and the quartz envelope is a good transmitter. All the radiation can be concentrated where it is needed, offering the heating equivalent in concentrated setups of a 1200-watt infrared source.

Further information may be had from Fisher Scientific Co., 717 Forbes St., Pittsburgh 19, Pennsylvania.

Storage Life of Sodium Nitroprusside Solution

Most sources of analytical chemistry recommend the use of freshly prepared solution of sodium nitroprusside in water when carrying out the color test with sulfide ion or a ketone. Kuppu Rao Vittal Rao and Arcot Viswanathan, of the Minerva Tutorial College, Madras, South India, have carried out tests with carefully prepared solutions of sodium nitroprusside in water and in methanol, kept in the laboratory in colorless and in amber bottles. All solutions have given satisfactory tests for at least as long as four months.

Audio Educational Material

Listings of records available for classroom instruction have been added to the 1954 edition of the "American Educational Catalog." Subject, title, publisher, author, grade, and price are given in these listings.

The "American Educational Catalog" contains lists of more than 12,000 textbooks and other teaching materials, giving subject and grade as well as an author index. It is now in its 83rd edition and can be obtained for $1 net postpaid from the R. R. Bowker Co., 62 West 45th St., New York 36, New York.

The Vapormaster

The Vapormaster, a portable ultraviolet analyzer for measuring minute quantities of gas in air is now available from the Manufacturers Engineering and Equipment Corp., Hatboro, Pennsylvania.

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A CHECKLIST OF WILEY BOOKS . . .

Successful Commercial Chemical Development

Edited by H. M. Corley, Armour & Co. The important principles by which new chemicals are selected and developed to the point of economic importance. *1954. Approx. 390 pages. Prob. $9.00.*

X-ray Diffraction Procedures

For Polycrystalline and Amorphous Materials

By Harold P. Klug and Leroy E. Alexander, both of the Mellon Institute. *1954. 716 pages. $15.00.*

Laboratory Experiments In Physiological Chemistry, *Second Edition*

By A. K. Anderson and Gordon H. Pritham, both of Pennsylvania State University. A revised and broadened edition of a reliable and widely useful manual designed to meet the requirements of a wide variety of laboratory courses. *In preparation.*

Introduction to Chemistry

By R. T. Sanderson, State University of Iowa. *1954. 542 pages. $5.50.*

Quantitative Organic Analysis via Functional Groups, *Second Edition*

By S. Siggia, General Aniline and Film Corp. ". . . a must for any chemist confronted with the problem of organic analysis."—*S.P.E. Journal. 1954. 227 pages. $5.00.*

Organic Chemistry, *Second Edition*

By R. C. Fuson and H. R. Snyder, both of the University of Illinois. *1954. 544 pages. $6.50.*

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Chemistry of the Defect Solid State. By A. L. G. Rees, of the Commonwealth Scientific and Industrial Research Organization, Melbourne. A Methuen Chemical Monograph. *1954. 136 pages. $2.00.*

The Biochemistry of the Nucleic Acids. Second Edition. By J. N. Davidson, University of Glasgow. A Methuen Biochemical Monograph. *1954. 200 pages. $2.25.*

Protein Metabolism. By R. B. Fisher, University of Oxford. A Methuen Biochemical Monograph. *1954. In preparation.*

The Infra-Red Spectra of Complex Molecules. By L. J. Bellamy, Ministry of Supply, U. K. *1954. In preparation.*

Minerals for the Chemical and Allied Industries. By Sydney J. Johnstone, Mineral Resources Department, Imperial Institute, London. *1954. 692 pages. $11.50.*

Qualitative Inorganic Analysis. By G. Charlot, École Supérieure de Physique et de Chemie Industrielle de Paris. *1954. In preparation*

Chemotherapy of Infections. By H. O. J. Collier, Allen & Hanburys, Ltd. *1954. 248 pages. $4.00.*

Yeast Technology. By John White, The Tower Yeast Co., Ltd. *1954. 432 pages. $8.00.*

Industrial Inorganic Analysis. By Roland S. Young, International Nickel Company of Canada, Ltd., New York. *1953. 368 pages. $5.75.*

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Complete details are available from the manufacturer.

New Literature

● A new 8-page folder on the Sigmamotor pumps is now available from Sigmamotor, Inc., 3 N. Main St., Middleport, New York. The folder illustrates and describes in great detail the design and operation of these pumps. Copies are available free on request.

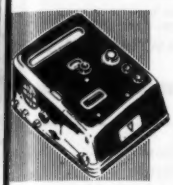
● A comprehensive catalogue on stopwatches has just been published by Clebar Watch Agency, 521 Fifth Ave., New York 17, New York. The new 1954–55 Clebar catalogue clearly illustrates and fully describes a stopwatch for every precision timing purpose. In all, the catalogue shows more than a score of stopwatches, timers and chronographs and has a special section on award and gift watches. An entire page is devoted to basic product advantages of the Clebar Watch, foremost of which is their patented spare parts compartment.

● The current issue of "Lanco Apparatus News" is now available from Arthur S. LaPine & Co., 6001 S. Knox Ave., Chicago 29, Illinois. This attractive 12-page bulletin contains data on some of the newest products for the laboratory.

● New air-cooled model high-vacuum oil-diffusion pump marketed by Bronwill Scientific, Inc., 45 Russell St., Rochester 7, New York, is described in an illustrated 4-page folder. It includes design, performance, and specification data plus details on Asco Laboratory Stirring Rod Gland and Asco Vacuum Gauge.

Spot News ...of the month

- **Coleman Universal Spectrophotometer Saves Money 3 Ways**



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● To meet the need for a more comprehensive list of hazardous gases and equipment recommended to protect against them, Acme Protection Equipment Co., Chicago manufacturers of gas masks, has just published the Acme Protection Guide for Hazardous Gases.

The tabulation shows a total of 433 gases, fumes, mists, and dusts present in operations where a gas mask should be worn. Included is descriptive information, limits for determining safe working conditions, and listing of the type of Acme canister designed for each specific hazard. For convenience of users, the Guide presents the gases in alphabetic divisions for quick and easy reference.

Free copies can be obtained direct from Acme Protection Equipment Co., 3037 W. Lake St., Chicago 12, Illinois.

● The significant principles and components of electronic data processing equipment are described in "Light on the Future," an illustrated booklet now available from International Business Machines Corp., 590 Madison Ave., New York 22, N. Y.

After a brief comparison of the construction and applications of analogue and digital computers, the booklet explains the organization of digital computers, and describes briefly the functions of the input, storage, arithmetic, control, and output components. A chart in the booklet compares the decimal numbers from zero to thirteen with the corresponding symbols in the binary system, which is used for the internal operations in many digital computers, although initial data and final results may be in the familiar decimal system. The booklet discusses the stored program concept and its advantages. A brief section discusses future possibilities in the field of electronic equipment, and the booklet concludes with a glossary.

● Barnstead Still & Sterilizer Co. now has ready for distribution its new Bulletin No. 131 which describes in detail the Barnstead Ventgard, an exclusive Barnstead product for protecting distilled water in storage from bacteria, dust, mist, and gases including CO_2.

This bulletin describes how the Ventgard may be attached to either a Pyrex or metal storage tank containing distilled water to filter the incoming air taken into the tank as the mater is drawn off.

The bulletin also gives details of laboratory tests made with the Barnstead Ventgard showing 100% efficiency even with particles as small as 0.2 micron thus giving complete purity protection to the water contained in storage tanks.

For your copy of Barnstead's Ventgard Bulletin No. 131 write to Barnstead Still & Sterilizer Co., 108 Lanesville Terrace, Forest Hills, Boston 31, Massachusetts.

● A 54-page booklet, "Research at ALCOA," has just been published by Aluminum Company of America. In addition to a description of the work of Aluminum Research Laboratories, it provides a 40-page bibliography of technical articles about aluminum.

Copies of the booklet may be obtained from Alcoa Sales Offices or from Aluminum Company of America, 726 Alcoa Building, Pittsburgh 19, Pennsylvania.

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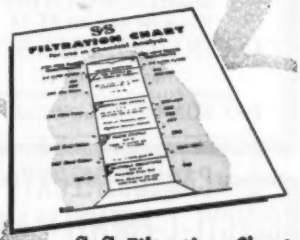
Detailed information and simple directions for use of membrane filters. This folder describes the new S&S "Bac-T-Flex"*, flexible membrane filter with a larger, green-colored grid designed for easier, more accurate bacteria count.



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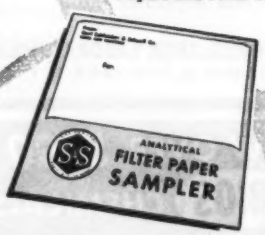
This wall-sized chart shows at a glance which filter paper to use for a given analysis. Gives relative retention values of S&S Analytical Filter Papers and other brands.



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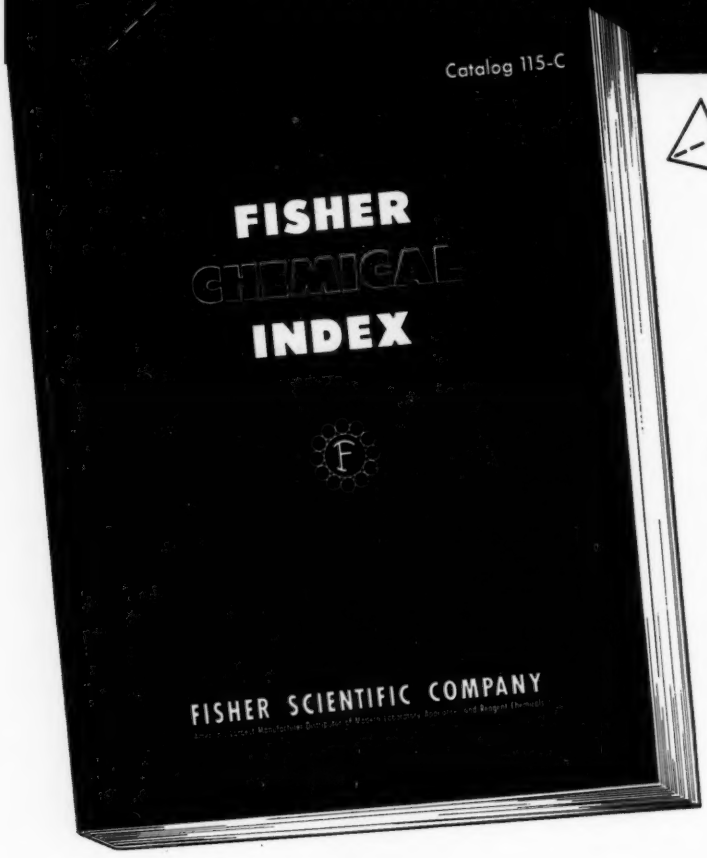

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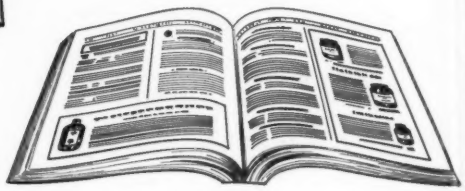

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